A Color-forming Reaction
in the System of Reversed Microemulsions

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Abstract

As a successive reaction, the color-forming reaction occurred in color photographic chemistry has been studied in AOT reversed micelles. As the beginning of the successive reaction, the oxidation of a color developer by the AgCl particle proceeds in the water pool of AOT reversed micelles. And a following color coupling reaction of the oxide for the color developer with a photographic color coupler proceeds on the interface of the surfactant and hydrophobic outer- phase of the reversed micellar system. The color dye thus formed, then distributed into the continued hydrophobic outer-phase of the reversed micellar system. The experiments showed here, the complicated successive reaction in the color photographic chemistry could be highly controlled by adjusting a surfactant concentration, the ratio of [H2O]/[surfactant] and reagents concentration in water pools of the reversed micellar system. These advantages, together with the ability to tailor freely the particle size of silver halide in reversed micelles, suggest a rich use to study a successive-micro-heterogeneous reaction occurred both in hydrophilic and hydrophobic phase of a microenvironment. Most importantly, the work here provides a possibility to study the photographic chemistry of silver halide in a completely unusual way.

Introduction

Reversed micellar systems are currently being explored for making ultrafine particles of various metal and semiconductors [1-3]. The formation of ultrasmall particles of silver halide in reversed micelles containing ionic or non-ionic surfactants has also been reported [4-6].

Reversed micelles can provide a favorable microenvironment for a photosensitization process. The photosensitization of colloidal TiO2 and AgCl particles in water-in-oil microenvironment by organic dyes has been studied in our laboratory [7-9] and by others [10]. In our knowledge, a successive microheterogeneous reaction in a reversed micellar system has not been clarified. Here, a color-forming reaction relating to the color photographic chemistry is studied in the AOT reversed micellar system.

Experiments

In the present work, the reversed micelles consist of the water pool in AOT as surfactant and isooctane as the continuous hydrophobic phase, $\omega=[H_2O]/[AOT]=10$. A photographic cyan color coupler (1×10^{-3} mol/L) was firstly dissolved in isooctane. The particles of silver chloride were prepared by mixing two individual reversed micelles both containing AOT -isooctane with the coupler and aqueous solution of either silver nitrate or potassium chloride (excess 1% or 10% relatively to silver nitrate). This reversed micellar system containing the AgCl particle in the water pool and the photographic cyan color coupler in the continuous hydrophobic phase can be stable for one month at room temperature. The representative TEM image of AgCl particles thus prepared on Formvar film is showed in Fig. 1. The average diameter of AgCl particles is about 10 nm. The particle seemed spherical under TEM.
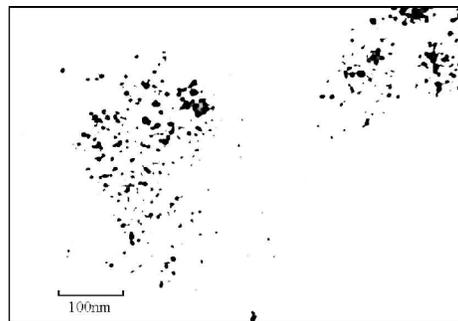
Fig.1. Transmission electron micrograph of the silver chloride sample in AOT reversed micelles.

The reversed micelle containing a color photographic developer in the water pool was independently prepared. The developer used in this work is a derivative of p-phenylene-diamine (CD-2, 4×10^{-4} mol/L).

Results and discussion

The successive reaction can be shown in the equation (1) to (3):

$$(CD-2) \qquad (QDI) \qquad (1)$$

$$(Cyan\ color\ coupler) \qquad (Leuco\text{-}dye) \qquad (2)$$
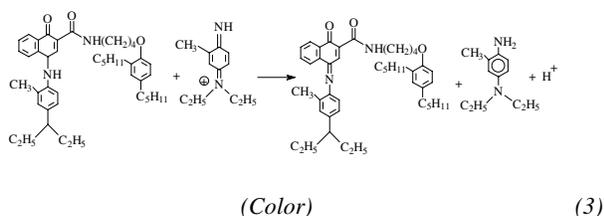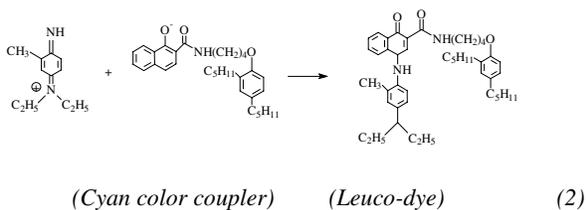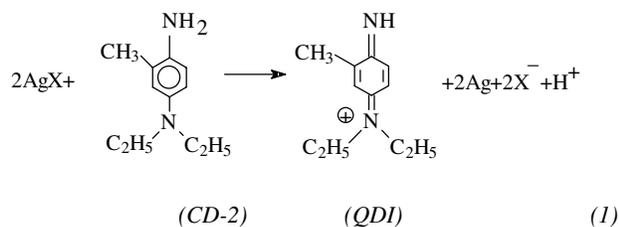
$$(Color) \qquad (3)$$

Replacing the cyan color coupler with yellow or magenta color coupler, a yellow or magenta color dye can form.

Fig.2 is a schematic diagram for the color-forming reaction occurred in the AOT-isooctane reversed micellar system. Several processes are included: (1) the reduction of AgCl into silver and the oxidation of CD-2 into quinonediimine (QDI) in water pools, (2) the formation of the cyan dye on the interface of the surfactant film and continuous hydrophobic phase of the reversed micellar system through the color coupling reaction between QDI and the cyan color coupler anions (equations 2 and 3); (3) the diffusion of cyan dye into continuous hydrophobic phase of the reversed micellar system; and (4) some of the basic system kinetic reactions including the collision among water pools, fusion-fission of the water pool and the intermicellar exchange of aqueous phase contents.

Obviously, the reactions in equations 1, 2 and 3 are redox reactions involving in electron transfer, therefore, the reactions are relatively fast. The time scale, however, for diffusion-controlled collision of micelles and for intermicellar exchange are respectively 0.1-1µs and 0.1-1ms[3]. Thus, the rate-limiting step of the color-forming reaction is assumed to be the intermicellar exchange of aqueous phase contents.

The color-forming reactions are followed by absorption spectra. Fig.3 is the spectral evolution of the reaction system
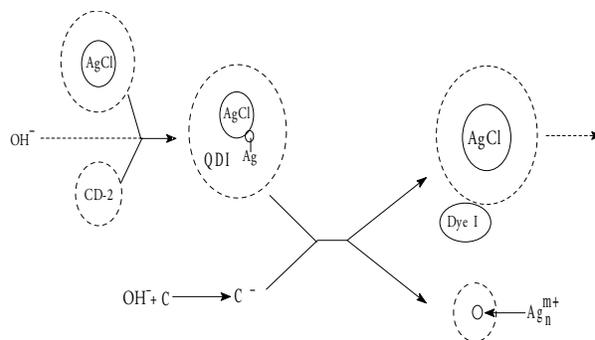
Fig.2. Schematic diagram for the color-forming processes occurred in the AOT-isooctane reversed micellar
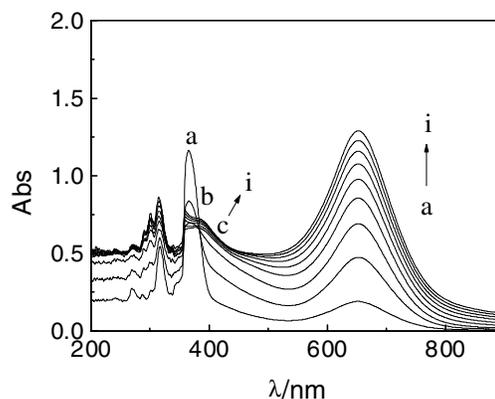
Fig.3 The absorption evolution during the color-forming reaction in reversed micelles, the reaction time for curves a to i is 5 to 45min, the time interval is 5 min.

with time. As shown in Fig.3, with increasing the reaction time, the absorption peak at 652nm increased. To compare with the absorption of the pure cyan dye formed from the CD-2 oxide and the cyan color coupler, it can be confirmed that the absorption at 652nm is the absorption of the cyan dye.

According to Pukies, Tausch-Treml, Henglein, Janata [11-14], and Zhu et al [15], the absorption peaks at 365, 315, 290 and 270nm in Fig.3 are preliminary assigned to Ag atom, Ag_2^+, Ag_3^{2+}, and Ag_4^{2+} clusters. And with increasing the reaction time, the absorption peak at 365nm decreased and peaks in the range of 250 to 315nm increased. In other words, as increasing time, the silver atom continues slowly to aggregate into small silver microclusters.

Based on the modes of Pileni [16] and Joselevich et al [17], the molar concentration of AOT micelles in the present work was about 2.4×10^{21} micelle/L (0.2mol/L, AOT). The molar concentration of the AgCl particle for the given concentration of silver nitrate, 4.3×10^{-4}mol/L, for

example, was 1.5×10^{17} particle/L. Thus, the probability finding one AgCl particle in one micelle was 6.2×10^{-5}. In our experiments, the CD-2 concentration was 1.1×10^{4} mol/L, i.e. 6.6×10^{19} molecule/L. The probability to find one CD-2 molecule in one micelle was 2.8×10^{-2}. Therefore, each micelle contains generally only one CD-2 molecule. If the CD-2 molecule distributed into the water pool with one AgCl particle, the redox reaction between CD-2 and AgCl can start in the presence of NaOH. According to equation (1), the oxidation of each CD-2 molecule produced only two silver atoms. When the second water pool containing one-developer molecule reacts with the above AgCl particle, two silver atoms produced previously may already separated from the initial water pool by fusion-fission of reversed micelles. For this reason, bigger silver clusters can only form through fusion-fission among micelles containing silver atoms. Due to the domination of probability, there was little possibility to form bigger silver clusters, AOT film may protect the small silver clusters from aggregation and make them stable.

The determination by TEM showed, after the color-forming reaction, no any particles in the sample can be observed. That means the silver clusters produced during the redox reaction may be too small to be detected by TEM. During normal color photographic development, however, a silver image, i.e. bulk silver is formed.
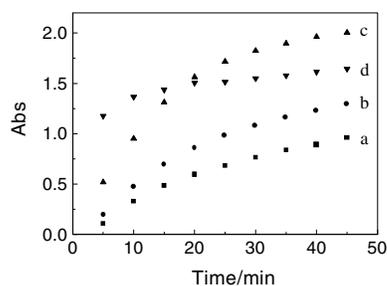
Fig.4. The change of the absorption at 652nm with reaction time. The detailed conditions are as following:

Curve	AOT Concentration (mol/L)	excess of Cl⁻	NaOH concentration (mol/L)
a	0.2	10%	0.002
b	0.2	1%	0.002
c	0.	1%	0.004
d	0.	1%	0.002

Various factors can influence the successive reaction. As shown in Fig.4, a decrease in AOT concentration leads to an increase in the rate of the dye formation. Keeping other parameters fixed, the decrease of AOT concentration leads to a decrease in the water pool concentration, which results in an increase of a reagent concentration in the water pool. An increase of Cl⁻ concentration leads to a decrease of the reaction rate, because Cl⁻ inhibits the reaction between AgCl and the developer.

As well known, the reduction of silver halide by a developer is a spontaneous process thermodynamically. Keeping other factors the same, a difference between developable and undevelopable grains of silver halide on a photographic film dynamically depends on the developing activity of a developer. During a normal color photographic development, the concentration of alkaline compounds in a photographic developer can influence the developing activity of a developer through effect on redox potential of the developer. Furthermore, in an alkaline solution, a cyan color coupler can form a coupler anion, which continues the color coupling-reaction with the oxide of a developer.

The experiments showed here, the concentration of sodium hydroxide is very important to start the color-forming reaction in the reversed micellar system. Even though the AgCl particles in reversed micelles are unexposed to light, the color-forming reaction still proceeds as long as the concentration of NaOH is suitable. And the more the concentration of NaOH is, the faster proceeds the reaction. On the chemical equation (1) to (3), the complete reaction for one-developer molecule needs two hydroxide ions to neutralize two protons. The hydroxide ions take part in the color-forming reaction here on stoichiometic relation.

Clearly, micelle solutions, particularly reversed micelles can offer a unique microenvironment, in which water-soluble reactants are isolated in different water pools and oil-soluble reactants present in a continuos hydrophobic phase. In reversed micellar system, a complicated color-forming reaction in photographic chemistry can be highly controlled by factors, such as a surfactant concentration, the ratio of $[H_2O]$/[surfactant], and a 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 a successive reaction occurred both in a hydrophilic and hydrophobic phase of a microenvironment. Most importantly, the work here provides a possibility to study the color photographic chemistry of silver halide in a completely unusual way.

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