

# Time-course Change of Electronic Spectra of Commercial Detergents with Rodamine 6G

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## ABSTRACT

The time-course changes of electronic spectra of aqueous solution containing commercial detergent and Rodamine 6G were studied at room temperature. The intensity of electronic spectra of fatty acid soap decreased with time. In case of synthetic detergents, the relationship between change of electronic spectra and time was not observed obviously because of the turbidity in solution. The surfactant micelle varies its structure with the passage of time.

## INTRODUCTION

Many investigations about the relationship between surfactants and dyes have been reported. Certain dye dissolved in the solution containing surfactant shows different colour in case below the critical micelle concentration (abbreviated as c. m. c. in what follows) of surfactant and in case above c. m. c..

It is called "metachromasis" that a adsorbed dye to surfactant shows different colour against the colour in existing in solution. Corrin, Harkins and Klevens determined c. m. c. of surfactants using this behavior. Electric conductivity method, viscosity method, surface tension method, light scattering method, solubilization method and osmotic pressure method were utilized to determine the c. m. c., and the colours method is well used because of its simplicity of use. The influences of salts<sup>2), 3)</sup>, and of alcohol<sup>4), 5), 6)</sup>, and of length of alkyl group<sup>7)</sup>, and of temperature<sup>8)</sup>, the c. m. c. of surfactants mixture<sup>9), 10), 11)</sup> and the c. m. c. of potassium alkyl mallo-nate<sup>12)</sup> were investigated.

In proceses of dyeing, it is time-consuming to get deeper colour and to raise the homogeneities in colour. There are few reports about the time-course change of interaction between dyes and surfactants as auxiliary in dyeing. It becomes populaly in laundering to wash clothes after soaking in detergent solution containing enzyme, but we can find few papers dealing with the time-course change of property of surfactant solution in such proceses.

Thus our interest has been paid on the relationship between the micelle amount and electronic spectrum. In this paper, a study on the time-course change of the property of surfactant micelle was made by the observation of electronic spectra of commercial detergents and Rodamine 6G.

## EXPERIMENTALS

### Materials

Commercial detergents summarized in Table 1 were used without purifications after pulverizing in a mortar. A is a fatty acid soap, B, C, D and E are synthetic detergents containing alkylbenzene sulfonate. Analytical grade Rodamine 6G (WAKO Pure Chemical) as colours was dissolved in water in a concentration of  $1 \times 10^{-3} \text{M}$  in each case when necessary. Ion-exchanged distilled water was used to dissolve these materials.

detergents	surfactants	builders	concentration indicated at laundry use
A	fatty acid soap	carbonate	0.16 %
B	$\alpha$ -olefin LAS	phosphate sulfate silicate	0.13 %
C	$\alpha$ -olefin LAS fatty acid soap	sulfate aluminosilicate silicate	0.13 %
D	LAS	sulfate aluminosilicate carbonate	0.15 %
E	SDS LAS	phosphate sulfate silicate aluminosilicate	0.13 %

Table 1. Compositions of commercial detergents.

### Measurements

A detergent was dissolved in  $40^\circ\text{C}$  water in a concentration of 2%. 1ml of  $1 \times 10^{-3} \text{M}$  Rodamine 6G solution was added into 100ml solution of detergent. Immediately after preparation of detergent solution, 1 hour after, 2 hours after, 3 hours after, 5 hours after, 7 hours after and 24 hours after, electronic spectra of these solutions were measured on a Hitachi 280A spectrophotometer at room temperature. In either measurement, freshly prepared Rodamine 6G solution was added to the solution in order to prevent the influence of decolouring of Rodamine 6G<sup>19)</sup>. The pH measurements were carried out with a TOA HM-18ET pH meter.

## RESULTS AND DISCUSSION

Pinacyanol chloride, Eosin, Sky Blue FF, Rodamine 6G and Na-Salt of 2,6-dichlorophenol-indophenol have been well used to determine the critical micelle concentration of surfactants. In general cationic colours are used for anionic surfactants, and for cationic surfactants anionic colours are well used. For example, Rodamine 6G shows a red colour in the region below c.m.c. and it fluoresces a orange colour above c.m.c..

With respect to colour change at c.m.c. Corrin and Harkins<sup>2)</sup> explain as follows; dye molecules associate when exist in water or in surfactant solution below c.m.c.. As surfactant micelles are formed only monomolecular dyes are adsorbed to micelles, in consequence the equilibrium between monomolecules and aggregates is shifted and the number of monomolecule increases on the whole. So the absorption spectrum is more closely to the spectrum of monomolecular state.

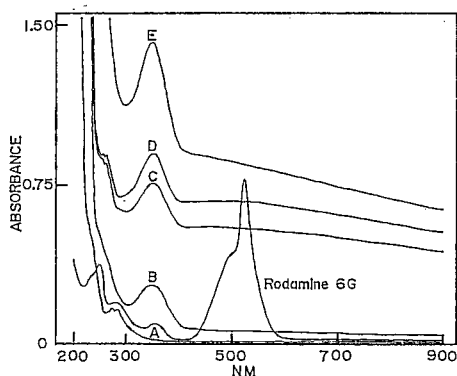


Figure 1. Electronic spectra of 0.2% commercial detergents and  $1 \times 10^{-5}$ M Rodamine 6G.

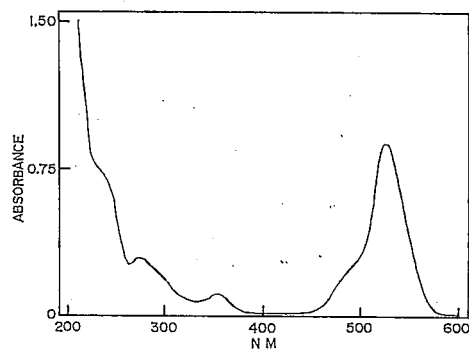


Figure 2. Electronic spectra of the solution containing 0.2% fatty acid soap and  $1 \times 10^{-5}$ M Rodamine 6G.

Figure 1 shows the spectra of 0.2% detergent solutions and of  $1 \times 10^{-5}$ M Rodamine 6G solution. Rodamine 6G solution exhibited its absorption maximum at 527nm and other peaks in the ultraviolet. On the other hand, commercial detergents, especially A and B had no absorption peak near 527nm but several peaks in the ultraviolet, C, D and E showed the overall increase of absorption owing to turbidity.

The electronic spectrum in the region of 200nm-600nm when Rodamine 6G was added to the fatty acid soap solution was shown in Figure 2.

It can be seen from Fig. 1 and Fig. 2 that the absorption maximum at 527nm is available to observe the time-course changes of interaction between surfactant micelles and Rodamine 6G molecules.

Figure 3 shows the time-course changes of spectra of 200nm-600nm in the case

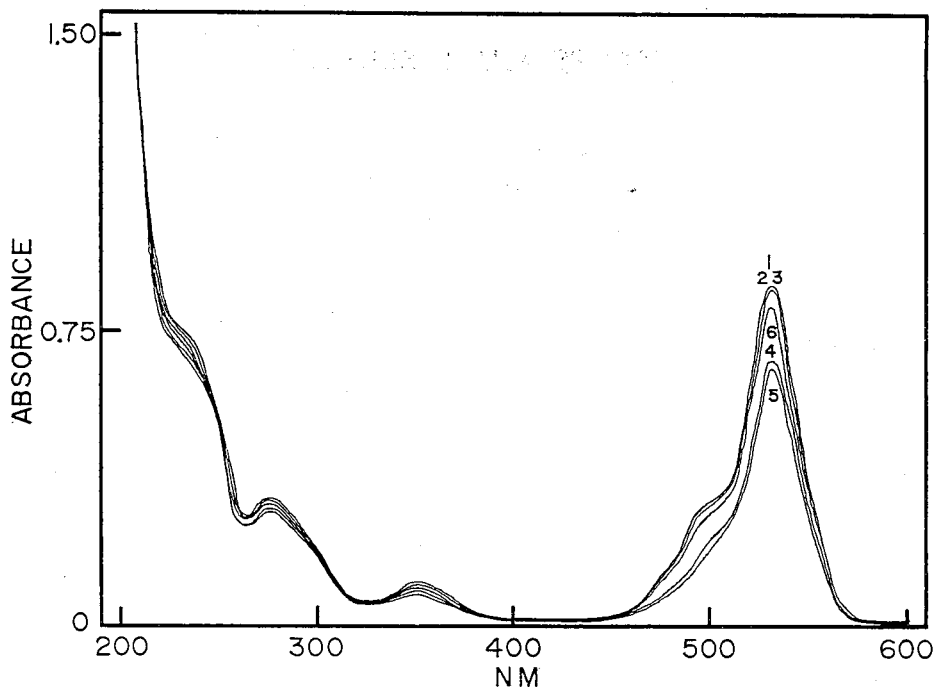


Figure 3. Time-course changes of electronic spectra of the fatty acid soap solution.  
 [Rodamine 6G] =  $1 \times 10^{-5} M$   
 1:0 hour 2:1 hour after 3:3 hours after 4:5 hours after  
 5:7 hours after 6:24 hours after

of Rodamine 6G addition to the fatty acid soap solution. As can be seen from this figure, the absorption intensities at 527nm decreased with the passage of time.

In the concentration region above c.m.c., 0.2% in this experiments, the equilibrium is reached between monomolecular state Rodamine 6G incorporated into the micelle and its molecular aggregates existing out of the micelle.

In these experiments Rodamine 6G solution was prepared newly just before use for each measurement. So the fact which the absorption intensity of electronic spectra decreased with time indicates that the quantitative change or structural change of the surfactant micelles occurs with the passage of time.

The time-course changes of absorption intensity of synthetic detergents and fatty acid soap were summarized in Table 2. Synthetic detergents C, D and E appeared turbidity when prepared, so the comparison of absorption intensity at 527nm was done as follows; the two trough points across the peak at 527nm were linked with straight line and the height from the line to the top of peak at 527nm was measured. Setting the height of line at zero hour as 1, the change of absorption intensity was expressed by ratio against the height at zero hour.

In case of fatty acid soap, the turbidity of solution was slightly observed after 24 hours, but the viscosity of solution increased and showed a gel state. The

detergents	ratio of absorption intensity at 527nm					
	0	1	3	5	7	24 hours
A	1	0.98	0.97	0.78	0.75	0.95
B	1	0.96	0.86	0.86	0.96	0.93
C	1	1.11	1.30	1.11	1.23	1.32
D	1	1.23	1.14	0.91	1.00	1.32
E	1	0.89	0.98	1.01	0.94	0.95

**Table 2.** Time-course changes in ratio of absorption intensity.

detergents	p H					
	0	1	3	5	7	24 hours
A	9.85	9.94	9.88	9.88	9.92	9.77
B	9.62	9.64	9.62	9.60	9.63	9.46
C	9.43	9.49	9.49	9.47	9.50	9.33
D	9.56	9.57	9.59	9.56	9.62	9.43
E	9.25	9.34	9.36	9.37	9.36	9.24

**Table 3.** Time-course changes of pH values.

structure of micelle in a gel state is attractive problem. The turbidity of synthetic detergent solutions became clearly with time and white precipitates were observed. This precipitates seemed to be silicate and enzyme as builder in detergents.

Table 3 shows pH changes of solution with the passage of time. The change in pH values was scarcely observed, therefore it seemed that the structure of micelle was little affected by hydrolysis.

Several structures of micelle have been proposed, but the relationship between the structure of micelle and the condition of solution is not so well-defined. Furthermore, it is poorly characterized that the micelle structure once formed is alterable or unalterable with the passage of time.

From the data shown in Table 2 it was suggested that the structure of micelle showed some change as time passage. Rearrangement of micelle structure between spherical, plates and columns state may occur. The measurement of micelle size by X-ray small angle scattering seems to give a significant information about the

time-course change of micelle structure.

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