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Kinetic Studies of the Reaction between Sodium Dodecyl Sulfate and Pinacyanol Chloride

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Below the critical micelle concentration, a kinetic study of the aggregate formation reaction of sodium dodecyl sulfate and pinacyanol chloride was made by means of a stopped-flow system combined with a rapid scanning spectrophotometer. The process involves the following four steps and a precipitate whose composition ratio was dodecyl sulfate : pinacyanol = 1 : 1 was obtained as the final product:

$$\frac{1}{2}D_2 \longleftrightarrow D \underset{S}{\rightleftarrows} DS \longleftrightarrow DS' \longleftrightarrow (\text{ppt})$$

where D and S are the dye and detergent molecules respectively. The forward rate constants have been calculated to be 6×10^5 (M s)$^{-1}$ for $[S]_0=0.05$—0.1 mM in the second step and 1.2×10^2—3.9×10^{-3} s^{-1} for $[S]_0=0.05$—1.0 mM in the third step.

Above the critical micelle concentration (CMC), the color of a mixed solution of sodium dodecyl sulfate (SDS) and pinacyanol chloride is characterized by two absorption bands, α at 615 nm and β at 570 nm.[1] These characteristic absorptions have been attributed to the incorporation of dye into the micelles.[1] In a kinetic study of that incorporation by the stopped-flow method, the absorption at the γ band, 480 nm, which is associated with dye-detergent salt,[1] appeared and reached its maximum within 1 ms. Its absorption gradually decreased with the time, while the absorption at the α band increased. From these results it was nearly proved that the dye is incorporated into micelles through an intermediate, dye-detergent salt. In view of the above considerations, the process of the dye-detergent salt formation should be observed by the stopped-flow method at lower concentrations of SDS. As a preliminary test, the dynamic behavior of the absorption spectrum over a wide range of wavelengths was observed using the stopped-flow system combined with a rapid scanning spectrophotometer. The change in the absorption at the γ band with the time could be observed as expected. Moreover, the absorption at the γ band decreased gradually with the time, while the absorption at 520 nm appeared and subsequently increased. Finally, this new absorption disappeared completely within one or two days.

The purpose of the present investigation is to study the kinetics of the overall reaction in which the salt precipitates after the solutions of pinacyanol chloride and SDS have been mixed below CMC, paying attention to the absorptions at the γ band 520 nm.

Experimental

Materials. The SDS and the pinacyanol chloride were obtained from Nikko Chemicals Co. and Eastmann Organic Chemicals Co. respectively. These reagents were used without further purification. The CMC of SDS was measured to be 7.6, 7.1, and 7.0 mM by the electrical conductivity, surface tension, and viscosity methods respectively, and was measured to be 5.7 mM in 0.02 mM of pinacyanol chloride by the spectral method at 20 °C.

Method. The dynamic spectra were measured by means of a stopped-flow system combined with a rapid scanning spectrophotometer, JASCO, RSP-1D, whose scanning speed was 400 nm/ms. This spectrophotometer, moreover, was also used as a fixed-wavelength monochromator. The dead time of the stopped-flow system was less than 2 ms.[2] All the experiments were performed at 25 °C.

Results and Discussion

The dependence of the static spectrum on the concentration of SDS was measured in a 0.04 mM solution of pinacyanol chloride, and very complex spectra were observed, as can be seen in Fig. 1. In the range of 0.1—3 mM of SDS, the absorption changed with the time, and a precipitate was observed on standing for a long time. Therefore, the measurement was done within one hour after mixing the pinacyanol chloride with the SDS. In the higher concentration range of SDS, no absorption change was observed even after 16 hours.

The stable peaks of absorption due to the incorporation of dye into the micelles were observed at the α and β bands, above the CMC. On the other hand, the quite stable peak of absorption, whose half-life period is greater than 6 hours, associated with the

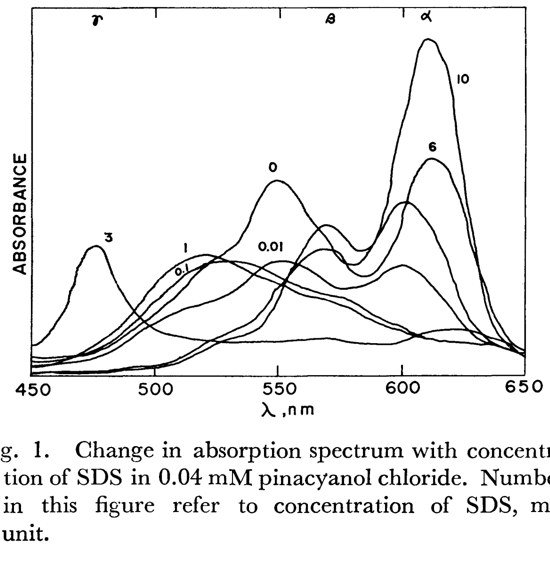

Fig. 1. Change in absorption spectrum with concentration of SDS in 0.04 mM pinacyanol chloride. Numbers in this figure refer to concentration of SDS, mM unit.

dye-detergent salt was observed at the γ band in about 3 mM of SDS. Further, in the lower range (0.1—1 mM) of SDS an unaccountable peak of absorption was observed at 520 nm. Below 0.1 mM of SDS, the characteristic absorptions of pinacyanol chloride were observed at 550 and 600 nm.

In the measurement of the dynamic spectrum, the characteristic absorptions of pinacyanol chloride at 550 and 600 nm in 0.1 mM of SDS decreased with the time, while that at the γ band increased after mixing, as is shown in Fig. 2. Subsequently, the absorption at the γ band gradually decreased with the time, while an unaccountable one at 520 nm appeared and increased. Finally, this absorption at 520 nm disappeared completely and the precipitate settled within one or two days. At a higher concentration, 0.25 mM, of SDS, the absorptions at 550 and 600 nm could not be observed, and that at the γ band reached its maximum within 1 ms after mixing, as is shown in Fig. 3. Subsequently, those at the γ band and 520 nm changed with the time in a manner similar to that in 0.1 mM of SDS. The above results lead us to presume that the species associated with the absorption at 520 nm is produced through the intermediate, the dye-detergent salt. In the meantime, at a lower concentration, 0.025 mM, of SDS, the absorptions at 550 and 600 nm gradually decreased with the time, while the absorption at 520 nm increased after mixing without any appearance of the absorption at the γ band, as can be seen from Fig. 4. These facts indicate that the formation rate of dye detergent salt is less than or equal to that of species associated with the absorption at 520 nm.

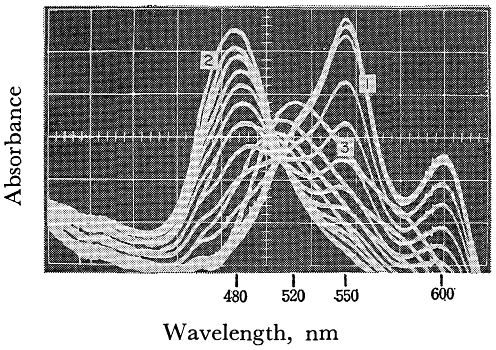

Fig. 2. Change in absorption spectrum with time. $[S]_0=0.1$ mM. $[D]_0=0.04$ mM. Time after mixing, 1 : 1 ms, 2 : 80 ms, 3 : 28 s.

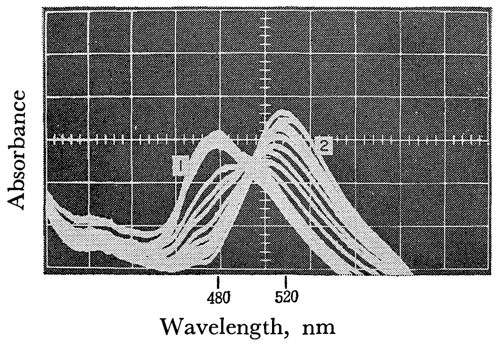

Fig. 3. Change in absoption spectrum with time. $[S]_0=0.25$ mM. $[D]_0=0.04$ mM. Time after mixing, 1 : 1 ms, 2 : 205 s.

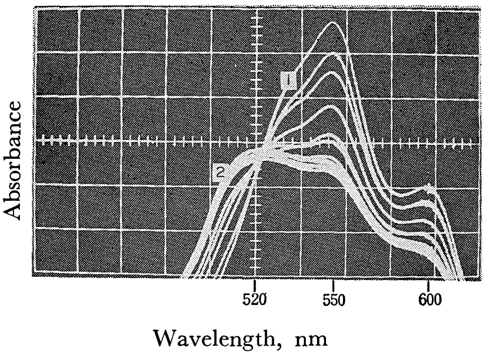

Fig. 4. Change in absorption spectrum with time. $[S]_0=0.025$ mM. $[D]_0=0.04$ mM. Time after mixing, 1 : 50 ms, 2 : 50 s.

Then, the changes in the absorptions at the γ band, 520, 550, and 600 nm with the time were measured in further detail at four fixed wavelengths by the stopped-flow method in 0.05 and 0.1 mM of SDS in order to study the overall reaction. The absorbances at 550 and 600 nm changed with the time after the mixing of 0.08 mM of pinacyanol chloride with 0.2 mM of SDS, as is shown in Fig. 5. Here, the dead time was 4 ms, since the mixing-flow time had to be lowered because the sample was a foamy liquid. As can be seen from Fig. 5, the variations in the absorbances at 550 and 600 nm with the time differ from each other in shape. In order to examine the above phenomenon in detail, the concentration dependences of absorptions at 550 and 600 nm were measured in an aqueous solution of dye alone. The plots of the absorbances at both wavelength *vs.* the total concentration of the dye are not linear, as can be seen from Fig. 6.

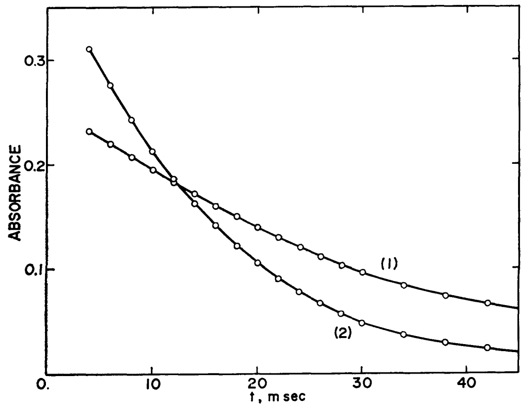

Fig. 5. Changes in absorbance with time. $[S]_0=0.1$ mM. $[D]_0=0.04$ mM. (1) : 550 nm, (2) : 600 nm.

It has been reported that, in a certain range of concentrations, a cationic dye is in equilibrium between the monomer and dimer.[3] Therefore, the following equilibrium for the present system can be assumed:

$$D_2 \rightleftharpoons 2D \qquad (1)$$

where D is the dye molecule. Then, the equilibrium

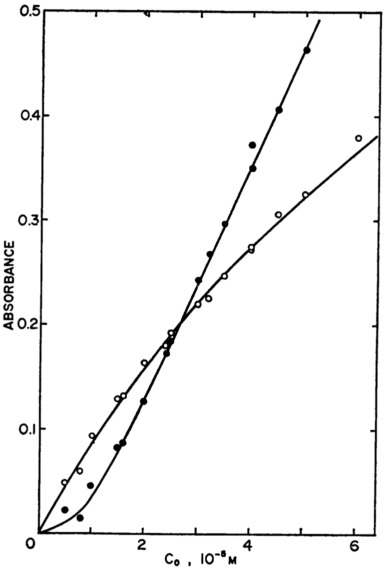

Fig. 6. Changes in absorbance with concentration of pinacyanol chloride. ●: 550 nm, ○: 600 nm.

constant K_1 is given by:

$$K_1 = 2\delta^2 C_0/(1-\delta) \tag{2}$$

where C_0 is the total concentration of dye in the monomer unit and δ, the dissociation degree. On the other hand, the absorbances, A, at the two absorption bands are given by:

$$A_D = \varepsilon_D C_D l = \varepsilon_D (1-\delta) C_0 l/2 \tag{3}$$

$$A_M = \varepsilon_M C_M l = \varepsilon_M \delta C_0 l \tag{4}$$

where ε is the molar absorption coefficient, l, the pass length of the cell, and the subscripts, D and M, refer to the dimer and the monomer respectively. The values of K_1, ε_D, and ε_M were determined so as to obtain the best fit of the data to the theoretical curves calculated by Eqs. (2)—(4). The theoretical curves, which are characterized by $K_1 = 2\times10^4$ M, $\varepsilon_D = \varepsilon_{550} = 3.8\times10^5$ M^{-1} cm^{-1}, and $\varepsilon_M = \varepsilon_{600} = 4.5\times10^4$ M^{-1} cm^{-1}, are shown in Fig. 6, along with the experimental data. The good fitting of the experimental and theoretical values indicates that the equilibrium of $D_2 \rightleftharpoons 2D$ is varied for the present system. The kinetic study for this step might be made by the chemical relaxation method.

Assuming that the dye-detergent salt is produced from SDS and the monomer of pinacyanol which is more reactive than the dimer, the formation of salt may be represented by:

$$mD + n_1S \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} X \tag{5}$$

where S is the detergent; X, salt; m and n_1, stoichiometric constants, and k_2 and k_{-2}, forward and backward rate constants respectively. Therefore, the formation rate of X is given by:

$$\frac{d[X]}{dt} = k_2[D]^m[S]^{n_1} - k_{-2}[X] \tag{6}$$

$$m[X] = [D]_0 - \left([D] + \frac{1}{2}[D_2]\right) \tag{7}$$

$$[S] = [S]_0 - n_1[X] \tag{8}$$

In an earlier stage of the reaction

$$\frac{d[X]}{dt} = k_2[D]^m[S]^{n_1} \tag{9}$$

and

$$\int_{[X]_i}^{[X]_t} d[X] = k_2\int_i^t [D]^m[S]^{n_1}dt \tag{10}$$

where i is the dead time. The two integers, m and n_1, were determined so as to obtain the best linear plot of the integration on the left *vs.* that on the right of Eq. (10). In both cases of $[S]_0 = 0.05$ and 0.1 mM, the assumption of $m = n_1 = 1$ was sufficient to give the best straight line, whose slope gave $k_2 = 6\times10^5$ (M s)$^{-1}$. Therefore, X can by represented by DS. In practice, the integration on the right was performed by the graphical method. The plot is shown for $[D]_0 = 0.04$ mM and $[S]_0 = 0.1$ mM in Fig. 7. The value of k_{-2} can be calculated theoretically from the deviation of the integration on the left-hand side of Eq. (10) from the straight line at the final stage of the reaction, but it could not be determined in practice because the values of [X] were not very accurate there.

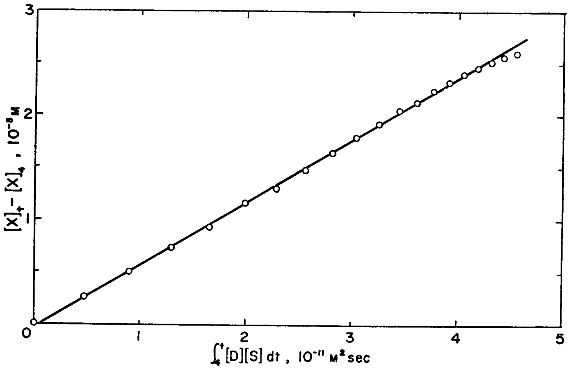

Fig. 7. A plot of $[X]_t - [X]_4$ *vs.* $\int_4^t [D][S]\,dt$. $[S]_0 = 0.1$ mM. $[D]_0 = 0.04$ mM.

Since the species, Y, associated with the absorption at 520 nm must be produced through the DS associated with that at the γ band, the formation of the former may be represented by:

$$n_2(DS) \overset{k_3}{\rightleftharpoons} Y \tag{11}$$

where k_3 is a forward rate constant and n_2, a stoichiometric constant. In an earlier stage of the reaction

$$-\frac{d[DS]}{dt} = k_3[DS]^{n_2} \tag{12}$$

$$[DS] = \beta A_\gamma \tag{13}$$

and

$$\log(-dA_\gamma/dt) = \log(k_3\beta^{n_2-1}) + n_2 \log A_\gamma \tag{14}$$

where A_γ is an absorption coefficient at the γ band and β, a constant. All the plots of $\log(-dA_\gamma/dt)$ *vs.* $\log A_\gamma$ were linear, and their slopes, n_2, were nearly equal to unity, as can be seen from Fig. 8. Therefore, the forward process may be described by an equation of a first-order reaction and the product, Y, can be represented by DS′:

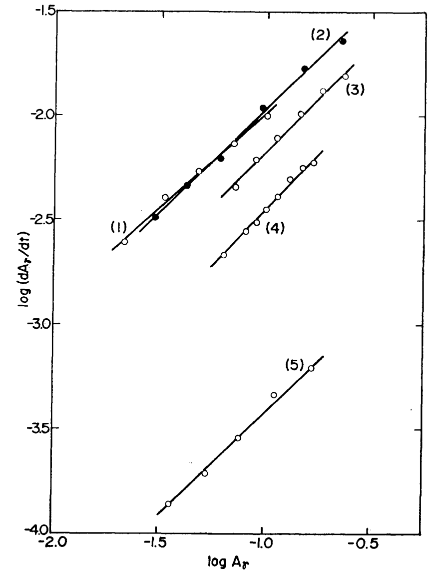

Fig. 8. Plots of log (dA_r/dt) *vs.* $\log A_r$. $[S]_0=0.05$—1.0 mM. $[D]_0=0.04$ mM. (1) : 0.05 mM, (2) : 0.1 mM, (3) : 0.2 mM, (4) : 0.5 mM, (5) : 1.0 mM.

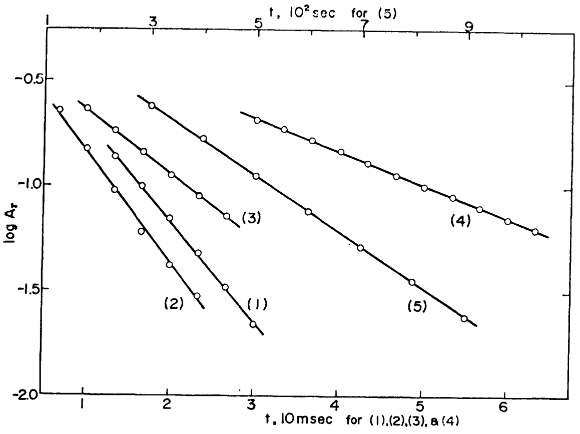

Fig. 9. Changes in $\log A_r$ with time. $[S]_0=0.05$—1.0 mM. $[D]_0=0.04$ mM. (1) : 0.05 mM, (2) : 0.1 mM, (3) : 0.2 mM, (4) : 0.5 mM, (5) : 1.0 mM.

$$DS \xrightarrow{k_3} DS' \qquad (15)$$

$$\ln A_r = -k_3 t + \ln A_{r0} \qquad (16)$$

The values of k_3 were obtained from the slope of the plots of $\ln A_r$ *vs.* t shown in Fig. 9; they are listed in Table 1.

When the absorption at 520 nm can be observed, as in the case described above, the salt precipitated completely within one or two days. The precipitate was recrystallized from ethanol to form large monoclinic needles, blue-violet in color. Microanalysis gave the results listed in Table 2 for both the recrystallized and unrecrystallized precipitates. Considering that both the analytical values are in good agreement with the theoretical ones calculated by assuming that the ratio of SDS and pinacyanol chloride is unity, the precipitate might be an aggregate of DS′ associated with the absorption at 520 nm:

TABLE 1. FORWARD RATE CONSTANTS FOR THE THIRD STEP REACTION

$[S]_0$, mM	k_3, s^{-1}
0.05	1.1×10^2
0.1	1.2×10^2
0.2	7.0×10
0.5	3.6×10
1.0	3.9×10^{-3}

TABLE 2. MASS RATIO OF ATOMS CONSTITUTING AGGREGATES OF SDS AND PINACYANOL CHLORIDE DETERMINED BY MICROANALYSIS

	N(%)	C(%)	H(%)
Unrecrystallized	4.53	71.81	8.14
Recrystallized	4.47	70.50	8.14
Calculated assuming [S] : [D]=1 : 1	4·28	71.05	8.15

$$n_3DS' \rightleftharpoons (DS')_{n_3} \qquad (17)$$

where n_3 is a stoichiometric constant. Consequently, the overall reaction may be given by:

$$\frac{1}{2}D_2 \rightleftarrows D \underset{S}{\rightleftarrows} DS \rightleftarrows DS' \rightleftarrows \frac{1}{n_3}(DS')_{n_3} \qquad (18)$$

Finally, although it should be noted that the forward rate constant in the third process decreases with the concentration of SDS except in 0.1 mM, no definitive conclusion can be drawn on the basis of the above experimental results alone. However, it may be presumed that the stability of DS increases with the concentration of SDS, while that of DS′ increases with the concentration of water. This, moreover, leads us to question whether DS is different from DS′ in the chemical bonding between D and S or is conformational isomers with DS′, which has a steric structure stabilized by a hydrophobic bonding.

References

1) P. Mukerjee and K. J. Mysels, *J. Amer. Chem. Soc.*, **77**, 2937 (1955).

2) T. Yasunaga, K. Takeda, and S. Harada, *J. Colloid Interfac. Sci.*, **42**, 457 (1973).

3) M. E. Lamm and D. M. Neville, Jr., *J. Phys. Chem.*, **69**, 3872 (1965).