

Studies on the Reaction Mechanism of Azo Dyes with Cetyltrimethylammonium Bromide

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The effect of salt addition to MO-CTB mixed micelle was studied. The logarithm of cmcs obtained from above experiment is a linear function of the logarithm of the sum of the cmc and the concentration of added salt.

In order to investigate the relation of the color change and the structure, the measurement of conductance to the mixed micelle has been carried out.

To see the color change and conductance data obtained in the present study, structure A is more probable one to the micelles having the λ_{max} 376nm.

The interactions between azo dyes and cationic surfactants have been known to give rise to a characteristic spectral change of the former in the visible and ultraviolet region¹⁻⁴⁾.

Hartley⁵⁾ studied the effects of anionic, cationic and non-ionic detergents on a large number of dyes.

Sheppard and Geddes⁶⁾ investigated changes in the absorption spectrum of pinacianol chloride in aqueous solution to which the cationic detergent cetylpyridinium chloride was added.

Corrin et al.⁷⁾ studied the effect of the addition of salts to aqueous solutions of colloidal electrolytes.

Klotz and Colleagues⁸⁾ showed that when MO is bound to cationic poly (ethylene imine) containing apolar side chains an absorption spectrum which is completely different from that exhibited by the same dye alone dissolved in water or in apolar solvents is observed.

Quadrifoglio and Crescenzi⁹⁾ found the new absorption band in colloids formed from interaction of the dye with cationic surfactants and with additional polycations.

They suggested that the band might arise from the thermally unstable cis-isomer of the dye which is some how stabilized in the bound state.

The cis- to trans- conversion of MO in aqueous solution is fast¹⁰⁾. When the dye

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is bound to protein, however, the acid catalyzed cis to trans-isomerization is slowed considerably.

Recently, Reeves and Harkaway¹¹ studied the interaction of the mixed micelles of methyl orange dye and cationic surfactants, and rejected the hypothesis of Quadrifoglio and Crescenzi with the results of irradiation experiments. They also presented three possible structures (A, B and C) of dye-surfactant mixed aggregates.

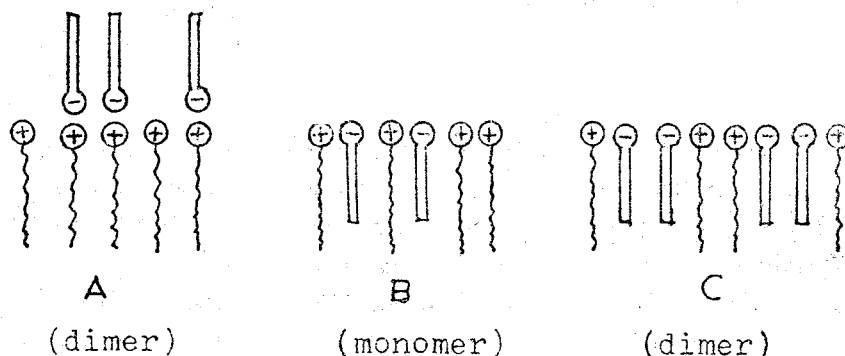


Chart 1— Possible structures of dye-surfactant mixed aggregates

Chart 1 shows possible partial structures of the mixed micelles. In all the structures, a high degree of charge neutralization by the oppositely charged head groups permits the mixed micelles to attain large size. In A type, the core of the micelle is formed by the more hydrophobic alkyl chains of the surfactant and the dye molecules are absorbed as oriented counterions. When it is remembered, however, that the bulk of the hydrophobic end of the dye molecule is nearly as great as that of the surfactant alkyl group, structure A would give a micelle with a hydrophobic surface and a stern layer in a region intermediate between the surface and the hydrocarbon core.

Any structure having the oppositely charged head groups in close proximity and the molecular axes of paired dyes reasonably parallel require that the hydrophobic moiety of the dye be turned completely outward into bulk water as in A, or completely inward as in B and C. Conductivity experiments have enabled us to reject the hypothesis of Reeves and Harkaway. We can draw some qualitative but comparatively detailed conclusions about the nature of the micelles.

The structure of absorption band near 376nm is presumed to A type rather than B type.

Experimental

The azobenzene derivatives were obtained from commercial sources, and were recrystallized several times from water or ethanol. Cetyltrimethylammonium bromide (Tokyo Kasei Co.) was recrystallized from ethanolic solution. Potassium chloride and potassium sulfate (Merck Co.) were used without further purification.

Other reagents were obtained from commercial sources. Absorption measurements were carried out with Unicam SP 1750 Ultraviolet Spectrophotometer connected to Unicam AR 25 Linear Recorder, using a 10-mm Quartz cell. The conductances of the solutions were measured in a cell (CEL-AO1) having a constant of 0.100cm^{-1} using a Beckman Instruments conductivity Model RC-18A attached to a thermostated water bath maintained at $25 \pm 0.5^\circ\text{C}$.

Results and Discussion

Absorption Spectra of MO and EO on the Interaction with CTB—The visible absorption spectra of MO in the presence of CTB show a marked spectral change. As shown in Fig. 1, the change of CTB concentration from $2 \times 10^{-5}\text{M}$ to $2 \times 10^{-3}\text{M}$ give rise to shift of λ_{max} from 465 to 370nm, 383 and 425 nm.

On going from the low concentration of added CTB to high concentration of CTB, there occur successively at least three types of spectra which can be distinguished clearly from one another as shown in above Figure.

Fig. 2 presents some typical data to illustrate the effects observed when the CTB concentration is progressively increased in $3 \times 10^{-5}\text{M}$ -EO solution. It is observed that when no CTB is present EO has an absorption peak at 475nm in water solution. As the CTB concentration is increased to a certain concentration, this peak at 475nm gradually decreases in absorbance and a new peak arises at around 395nm. Increasing the CTB concentration beyond $2 \times 10^{-4}\text{M}$, the absorption peak shifts to higher wavelength again. The absorption centered near 475nm is characteristic of the microcrystallites and absorption near 395 nm is from the mixed micelles between EO and CTB. Curve 3 of Figure 2 is typical pattern of suspension solution of particles and Curve 4 is characterized by principal absorption of the mixed micelle due to the dye stacking interaction. The mixed micelle is given at the concentration far below the cmc for the surfactant homomicelles by aqueous solution of EO and CTB.

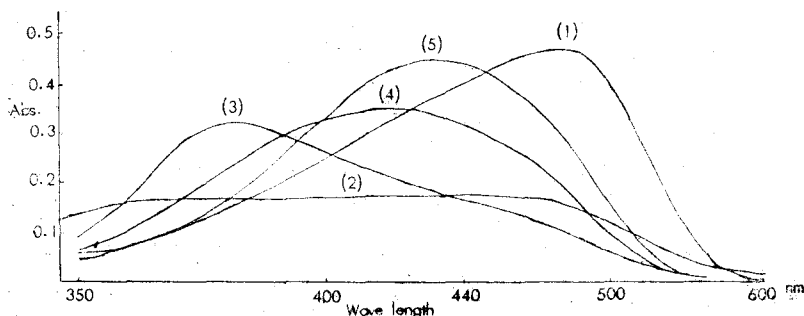


Figure 1—Absorption spectra of MO in several CTB concentrations.

MO: $2 \times 10^{-5}\text{M}$

CTB: (1) $2 \times 10^{-5}\text{M}$, (2) $2 \times 10^{-4}\text{M}$, (3) $8 \times 10^{-4}\text{M}$, (4) $1.5 \times 10^{-3}\text{M}$, (5) $2 \times 10^{-3}\text{M}$

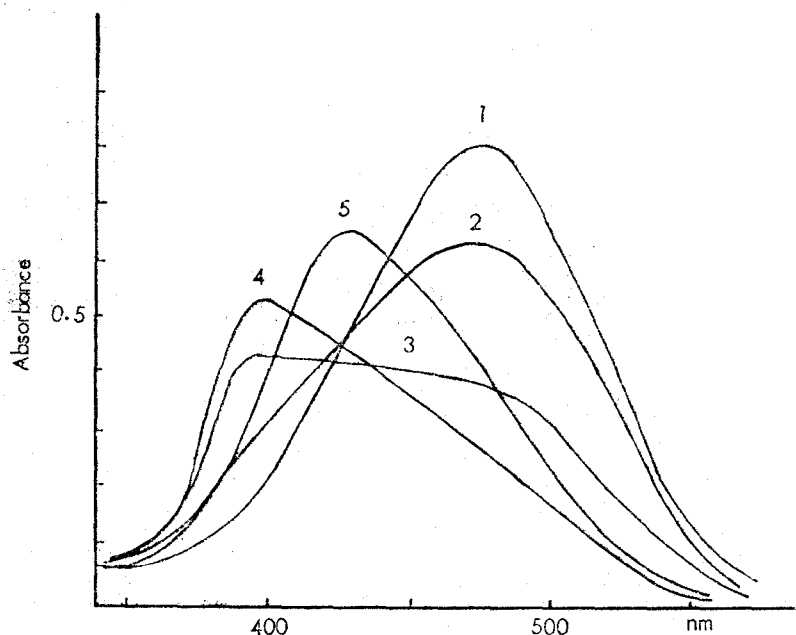


Figure 2—Absorption spectra of EO in several CTB concentrations.

EO: $3 \times 10^{-5} \text{M}$.

CTB: (1) 0, (2) $2 \times 10^{-5} \text{M}$, (3) $4 \times 10^{-5} \text{M}$, (4) $2 \times 10^{-4} \text{M}$, (5) $4 \times 10^{-3} \text{M}$.

The Effect of Salt Addition to the Mixed Micelle—In the absence of added salt an aqueous solution of MO ($3.3 \times 10^{-5} \text{M}$) and CTB ($3.3 \times 10^{-4} \text{M}$) has an absorption maximum at around 376 nm. When $3.3 \times 10^{-3} \text{M-K}_2\text{SO}_4$ or KCl is added in aqueous solution of MO and CTB, the absorption maxima shift to 426 and 386 nm, respectively. The red shifts of the absorption maxima in the presence of salts are identical with the changes obtained from increasing the surfactant concentration.

The changes of λ_{max} when salts added to an aqueous solution of MO-CTB are tabulated in table 1-2 and plotted in Fig. 3.

As known to see the figures, the steepest point of the curve is approximately 400 nm. The concentrations of K_2SO_4 and KCl salt in the steepest portion of the curves are $3.3 \times 10^{-4} \text{M}$ and $3.3 \times 10^{-3} \text{M}$, respectively, under the presence of $3.3 \times 10^{-4} \text{M}$ -CTB. Based on above the curve's pattern, it can be known that the effect of K_2SO_4 addition to MO-CTB solution is larger than in the case of KCl addition.

Accordingly, salts promote the spectral shift of absorption maximum and decrease critical micelle concentration for the mixed micelle as well as cmc for the surfactant

homomicelles. This trend is in agreement with the result of Herzfeld¹²⁾. It was reported that the cmc for CTB homomicelle is $9 \times 10^{-4} \text{M}$ at 25°C ¹³⁾.

In our study the cmc of CTB for the mixed micelle is about $7 \times 10^{-4} \text{M}$ in the presence of $3.3 \times 10^{-5} \text{M}$ -MO and no added salt. It is because the charge neutralization in the micelles by the oppositely charged head groups of dye and surfactant provides micellar stabilization without the need for a high degree of counterion binding and the reduced charge repulsion in the mixed micelles containing a small excess of surfactant permits the micelles to exist at much lower amphiphile concentrations than are possible for homomicelles¹⁴⁾. The λ_{max} obtained when a various concentrations of salts and CTB are added to a constant dye concentration of $3.3 \times 10^{-5} \text{M}$ -MO or $3 \times 10^{-5} \text{M}$ -EO are plotted as salt concentration versus CTB concentration. The concentration of added salts used in this work, the cmcs of CTB in the presence of salts and S/D ratio obtained from this work are summarized in Table 3 and 4.

The cmcs obtained by salt addition are introduced in equation of Corrin and Harkins¹⁵⁾.

In Fig. 4, $\log (C_o + C_{salt})$ in X-axis is plotted against $\log C_o$ in Y-axis.

Table 1 — λ_{max} of MO-CTB Mixed Micelle by Addition of K_2SO_4 (nm)

$\text{K}_2\text{SO}_4(\text{M})$	CTB												
	$\times 10^{-5} \text{M}$					$\times 10^{-4} \text{M}$							
	1	2.5	3	4	5	1	2	3	4	5	6	7	8
1×10^{-5}	465	374	375	374	374	375	374	374	374	374	416	423	425
3×10^{-5}	465	374							374	384	422	425	425
5×10^{-5}	465	374			374				374	384	426	425	425
7×10^{-5}	465	374								422	427	425	425
9×10^{-5}	465	$\frac{374}{455}$								388	422	424	
1×10^{-4}	465	455	$\frac{375}{455}$		374	375	374	374	417	425	425		430
3×10^{-4}	465					375	375	374	425		425		430
5×10^{-4}	465				374	375	374	389	425				
7×10^{-4}	465	459				375	375	419	425		425		
8×10^{-4}	465					375	375	421	425				
9×10^{-4}	465					375	375	425	425		425		
1×10^{-3}	465	454		375		375	375	425	425		430		
2×10^{-3}	465	454		375		375	389	425	425				
4×10^{-3}	465	454	$\frac{375}{455}$		375	376	425	426					
6×10^{-3}	465	456	$\frac{375}{455}$		376	375	425						
8×10^{-3}	465	457	376		376	375	425						
1×10^{-2}	463	457	455		376	383	425						

MO: $3.3 \times 10^{-5} \text{M}$

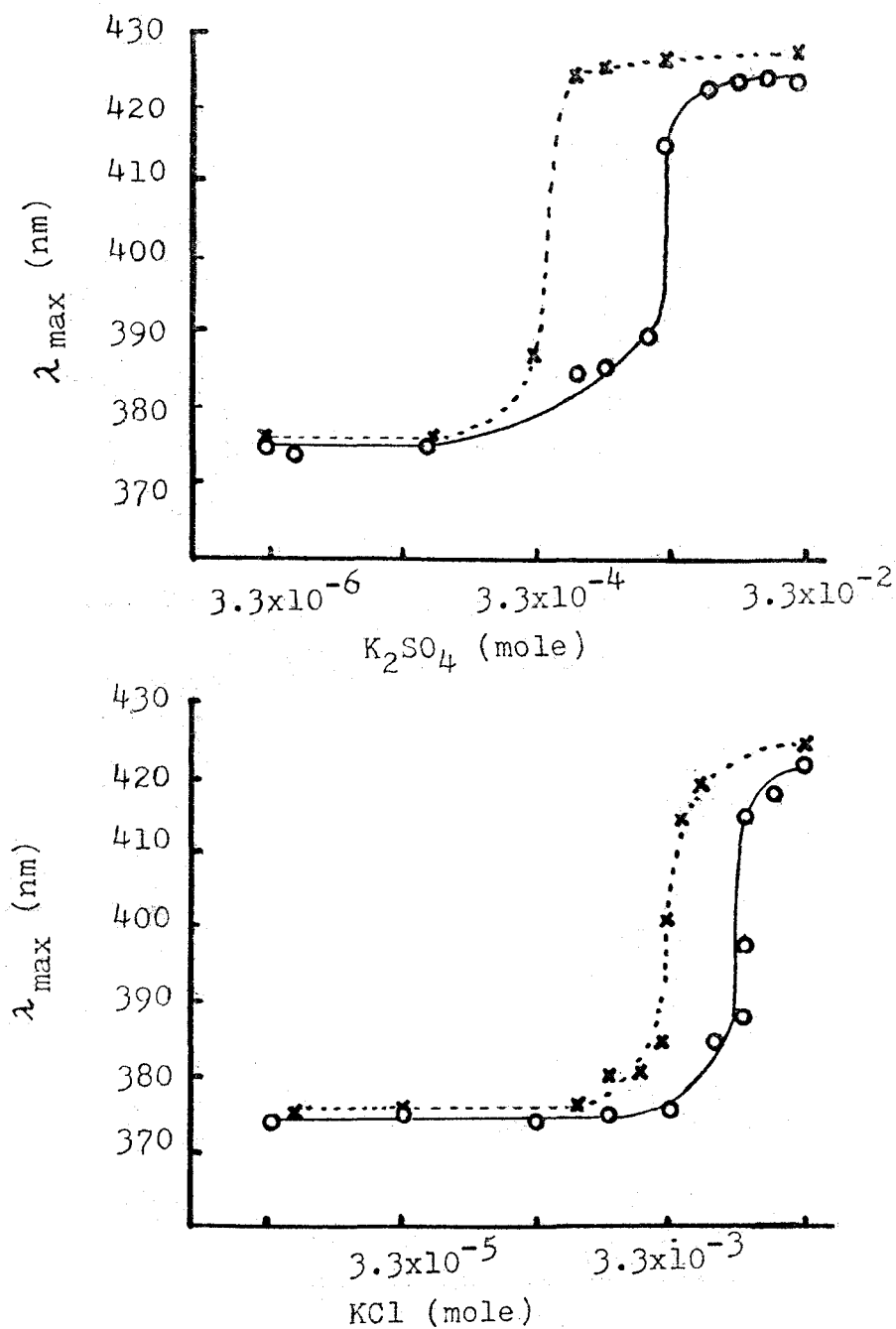


Figure 3— Change of λ_{max} by salt addition to MO-CTB solution.
 Key: O, CTB, $2 \times 10^{-4} M$; x, CTB, $3.3 \times 10^{-4} M$.

Table II— λ_{max} of MO-CTB Mixed Micelle by Addition of KCl (nm)

KCl(M)	CTB												
	$\times 10^{-5}M$					$\times 10^{-4}M$							
	1	2.5	3	4	5	1	2	3	4	5	6	7	8
1×10^{-5}	462	458	$\frac{375}{409}$	374	374	375	375	375	376	383	410	404	425
3×10^{-5}	462	455			374				375				425
5×10^{-5}	462	456		375	375				375				425
7×10^{-5}	462	455			375				375				425
9×10^{-5}	462	455		375	375				375				425
1×10^{-4}	462	455	$\frac{375}{382}$		375	375	375	375			412	421	425
3×10^{-4}	462				375	375	375				410	425	
5×10^{-4}	462						375	375			417		
7×10^{-4}	462	456			375			375					
8×10^{-4}	462					375	375	375	381			425	425
9×10^{-4}	462				375	375	375						
1×10^{-3}	462	455	$\frac{375}{364}$		375	375	375	390	402	422	425	425	
2×10^{-3}	462		364		375	375	375						
4×10^{-3}	462				375	375	386		413				
6×10^{-3}	462	455			375	375	415						
8×10^{-3}	462	455			375	378		401					
1×10^{-2}	463	455	375		376	375	375	420	425	425			

MO: $3.3 \times 10^{-5}M$ **Table III**—The cmcs of CTB for the Mixed Micelle in the Presence of KCl at 25°C

Concn. of KCl(M)	CMCS(M)	S/D(cmc of CTB/concn of MO)
0	7×10^{-4}	24.2
1×10^{-5}	5.2×10^{-4}	15.5
5×10^{-5}	4.7×10^{-4}	14.5
1×10^{-4}	4.6×10^{-4}	13.6
5×10^{-4}	4.1×10^{-4}	13.0
1×10^{-3}	3.9×10^{-4}	12.1
5×10^{-3}	3.0×10^{-4}	9.1
1×10^{-2}	2.2×10^{-4}	6.7

The result from the straight line led to the first order equation is similar to that obtained from anionic or cationic surfactant homomicelle in the presence of salts by other researchers^{17,18,19}.

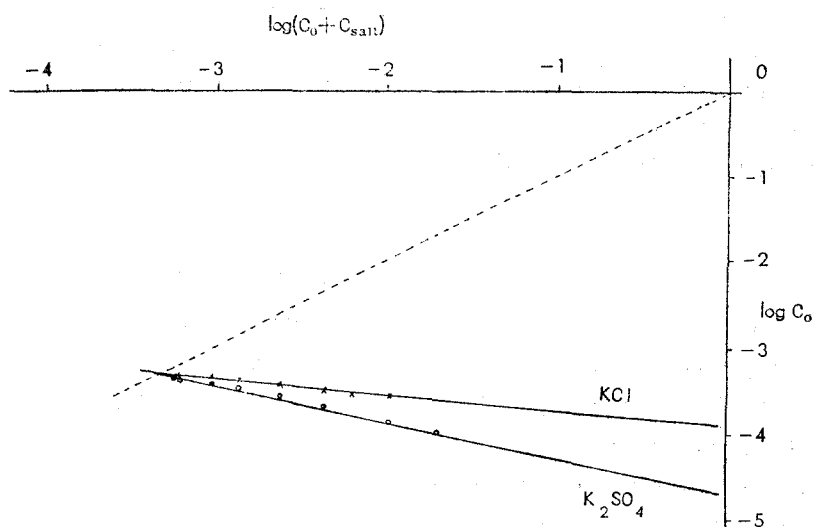
Accordingly, the effects of salt to MO-CTB are given by following equation.

$$\text{MO: } \log C_0 = -0.19 \log(C_0 + C_{kcl}) - 3.91$$

$$\log C_0 = -0.4 \log(C_0 + C_{K_2SO_4}) - 4.65$$

Table V—The cmcs of CTB for the Mixed Micelle in the Presence of K_2SO_4 at 25°C

Concns. of K_2SO_4 (M)	CMC(M)	S/D(cmc of CTB/concn. of MO)
0	7×10^{-4}	24.2
1×10^{-5}	5.1×10^{-4}	15.5
5×10^{-5}	4.3×10^{-4}	14.2
1×10^{-4}	4.1×10^{-4}	12.1
5×10^{-4}	3.3×10^{-4}	10.0
1×10^{-3}	2.6×10^{-4}	8.2
5×10^{-3}	1.4×10^{-4}	4.2
1×10^{-2}	1.0×10^{-4}	3.0

**Figure 4**— Plots of $\log (C_o + C_{salt})$ versus $\log C_o$

$$EO: \quad \log C_o = -0.33 \log (C_o + C_{KCl}) - 4.96$$

$$\log C_o = -0.41 \log (C_o + C_{K_2SO_4}) - 5.29$$

Where C_o is the cmc of CTB for the mixed micelle and C_{KCl} is the concentration of added KCl in moles per liter.

The logarithm of the cmc is a linear function of the logarithm of the sum of the cmc and the concentration of added salt.

Conductance Measurement—To see the results of λ_{max} measurement, the λ_{max} shift on changing the maximum absorption wavelength from 465nm to 376 nm is very fast, but the λ_{max} shift from 376nm to 425nm is slow.

In other words, the change of color from red to green is fast, but the change of color from green to yellowish-orange is slow. Thus, Reeves and Harkaway assumed that the structure having λ_{max} around 376 nm is stable. But this structure

Table V—Changes of Conductance by K_2SO_4 and CTB Addition to a Constant Concentration of MO($3.3 \times 10^{-5}M$) ($\times 10^{-5}\Omega$)

CTB(M)	K_2SO_4 (M)						
	1×10^{-4}	3×10^{-4}	5×10^{-4}	6×10^{-4}	8×10^{-4}	9×10^{-4}	1×10^{-3}
1×10^{-5}	2.9	7.7	13.1	15.7	21.0	23.3	25.8
3×10^{-4}	4.7	9.5	14.7	17.1	22.6	25.6	28.2
8×10^{-4}	9.4	13.5	18.9	22.1	26.9	29.3	34.7
1×10^{-3}	10.4	14.1	19.0	22.2	27.8	30.1	37.7

having λ_{max} 376nm (dimer) is different from the free MO(monomer), and such a structural change is expected to give rise to a marked conductance change.

If the structure having λ_{max} 376 nm is C type(dimer) presented by Reeves & Harkaway, such a structure of micelle is appreciably stable. And so the conductance change by salt addition may be not appeared markedly.

But, if it has the structure of A type(unstable), the change of conductance by salt addition occurs until the stable structure of B type(monomer) is formed.

The absorption curve of dye monomer in water has been presented by Reeves *et al.*¹⁶⁾.

In our study, the conductances of the mixed micelles were measured at 25°C after the same volume of a constant concentration of surfactant and K_2SO_4 were added to the same volume of MO($3.3 \times 10^{-5}M$), respectively.

The values obtained from the addition of surfactant and K_2SO_4 to methyloange are reported in Table 5.

In order to compare salt effects on the mixed micelle, it is convenient to plot the conductances obtained from the above experiment on the graph of the concentration of salt against the concentration of surfactant.

By connection of the same values of conductance, the significant feature is appeared as Fig. 5.

As shown in Fig. 5, the conductances for the mixed micelle decrease with increasing the concentrations of CTB when λ_{max} is changed from 465 nm to 376 nm. But the change of conductance is not appeared almostly when λ_{max} is changed from 376 nm to 425nm.

Regions of the mixed micelles having unpaired dyes (B type) probably exist in the micelles containing a large excess of surfactant, but structure A is more probable one for the micelles giving the absorption band near 376nm with the results of electroconductivity and spectrophotometry used in this present study.

To clarify the reaction mechanism of salt on the surfactant binding of Azo dyes, further study is required to understand the interaction with changing the parameters of surfactant or dye in the various pH state.

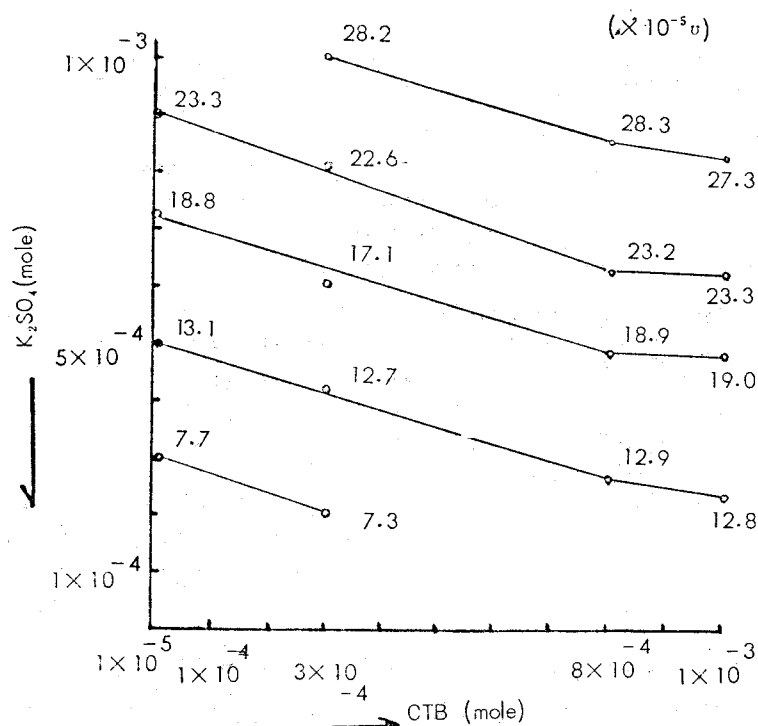


Figure 5—Decreasing trend of conductance for a constant concentration of CTB and salt added in the presence of MO($3.3 \times 10^{-5}M$).

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