

Studies on the Interaction of Azo Dyes with Cationic Surfactant (I)

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Abstract □ As the cetyltrimethyl ammonium bromide (CTAB) concentration increases to $2 \times 10^{-4} M$ the absorption maximum of ethyl orange (EO) makes a blue shift from 475nm to 395nm. At higher concentration of CTAB than $2 \times 10^{-4} M$ the absorption maximum shifts to higher wavelength than 395nm. A new peak at 395nm is shown to result from the mixed micelle due to dye stacking interaction rather than from a change in dye geometry. Because Raman spectra of EO on interaction with varying amount of CTAB are similar to that of EO in water, EO retains trans azo type on interaction with CTAB. There is a change of c.m.c.s of CTAB for the mixed micelle in the presence of salt. The effect of added salt on c.m.c. of CTAB for the mixed micelle is given that the logarithm of the c.m.c. is a linear function of the logarithm of the sum of the c.m.c. and the concentration of added salt.

Keywords □ CTAB, EO, Resonance Raman spectrum, Critical micelle concentration for the mixed micelle of CTAB and EO

Dye have all the characteristics of their color changes in dye systems when present in solution along with proteins or surfactants. The color change results in the shift of the first electronic absorption band to low wavelengths. This is caused by the unusual properties of the polymeric forms⁷⁾ of dyes

with proteins or surfactants. The study of these properties has produced information to describe the possible type of interaction between enzymes and substrates or inhibitors and the chemical nature of the binding site of proteins and other macromolecules.

Hartley¹⁾ studied the effects of anionic, cationic and non-ionic detergents on a large number of dyes. He demonstrated that the greatest color change occur when the charge on the detergent is opposite to that on the indicator ion. Subsequently, Sheppard and Geddes²⁾ investigated changes in the absorption spectrum of pinacyanol chloride in aqueous solution to which the cationic detergent cetylpyridinium chloride was added. Their study which was preliminary in nature, was greatly extended by Harkins et al.³⁾, whose investigations led them to develop a method for determining the critical micelle concentration of detergents utilizing the spectral changes produced in various dye solution. In the vicinity of the critical micelle concentration there was reported to be an abrupt change in the color of the indicator. Also they studied the effect of the addition of salts to aqueous solutions of colloidal electrolytes.⁴⁾ The behavior of the micellar aggregates present was not governed by the

principle of ionic strength or the Debye-Hückel relationships and related only to the concentration of that ion of an added salt which bears a charge opposite to that on the colloidal aggregate.

Recently Klotz and colleagues⁵⁾ showed that when MO is bound to cationic poly(ethyleneimine) 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. They attributed this behavior to the stacking of dye molecules bound to the apolar acyl groups. Quadrioglio and Crescenzi⁶⁾ found the new absorption spectrum in colloids formed from interaction of the dye with cationic surfactants and with additional polycations, but the new spectrum of the type observed by Klotz et al. was not found on interaction with all polycations. They suggested that when dye is bound to polyion under certain given conditions, the new spectrum might not be simply due to dye stacking on the polyion but arise from the thermally unstable cis isomer of the dye which is somehow stabilized in the bound state.

In this paper we elucidate the geometric change of dye bound to surfactant by means of resonance Raman spectroscopy and the effect of salts in the mixed micelles of the anionic dye and cationic surfactant by absorption measurements. Resonance Raman spectroscopy is the most appropriate tool to study the mixture of dye in aqueous environment and at concentration of approximately 10^{-5} or 10^{-6} M. As spectrometric

probes ethyl orange (EO, an anionic azo dye) and cetyltrimethyl ammonium bromide (CTAB, a cationic surfactant) were employed. Ethyl orange possesses a relatively simple structure and has a very high absorptivity. It makes less microcrystalline at concentration below the critical micelle concentration than MO. Cetyltrimethyl ammonium bromide has little effect on the pH of a solution. Therefore a large variation of concentration can be made and its micelle will be stable. And a dilute aqueous solution of EO and CTAB has an electronic absorption band around 475nm, and gives rise to the resonance Raman effect for the exciting wavelengths of 488.0 nm of an Ar⁺ laser.

EXPERIMENTAL

Measurements

Raman spectra were obtained using Jasco R-300 Resonance Spectrometer with 150mW of Ar⁺ laser power at 488.0nm. The spectral slitwidth was 450 μ m for the 488.0nm excitation. Raman spectra were recorded between 1000 and 1800 Cm^{-1} . Aqueous sample was circulated in a 1-mm capillary tube to prevent the rapid deterioration of the sample in the laser beam. The concentrations used in the resonance Raman study are equal to those used in the absorption study. Ultrafiltrations were done through milipore filter with uniform pore size of 0.45 μ m.

Absorption measurements were carried out with Unicam SP 1750 Ultraviolet Spectrophotometer connected to Unicam AR25

Linear Recorder, using a 10-mm quartz cells. The temperature at which the measurements were made was maintained at $25 \pm 0.5^\circ\text{C}$.
Meaterials and Solutions

All the products used are commercially available. Ethyl orange (EO) was from Kishida Chemical Ltd. It was purified by repeated crystallization from ethanol. It was prepared $9 \times 10^{-5}\text{M}$ in deionized water ($1.2 \times 10^{-6}\text{mhos/Cm}$) as stock solution and was diluted to required concentration.

Cetyltrimethyl ammonium bromide (CTAB) purchased from Tokyo Kasei Co. Ltd. was purified by reprecipitation from ethanol solution on adding ether. Surfactant solutions were prepared daily to the desired concentration.

Potassium chloride and potassium sulfate were products of Merck A. G., used without further purification.

RESULTS AND DISCUSSION

Absorption Spectra of EO on Interaction with CTAB

The spectra of EO solutions vary markedly with increasing concentration of CTAB. Figure 1 presents some typical data to illustrate the effects observed when the CTAB concentration is progressively increased in $3 \times 10^{-5}\text{M}$ EO solution.

In this graph the absorbance of the solution is plotted as a function of the wavelength. The various curves are for the concentrations of CTAB listed in the legend.

It is observed that when no CTAB is present EO has an absorption peak at 475nm in water. As the CTAB concentration is

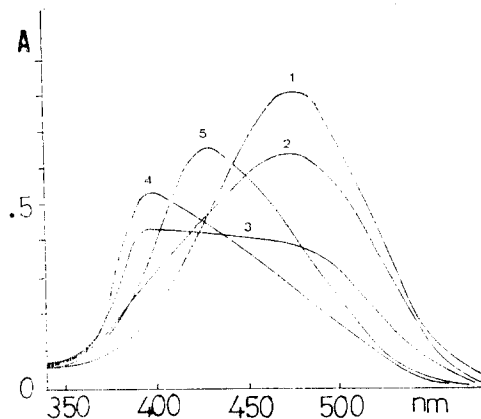


Fig. 1: Absorption spectra of EO in several CTAB concentration.

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

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

increased to a certain concentration this peak at 475 nm gradually decreases in absorbance and new peak arises at 395nm. Increasing the CTAB 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 395nm is from the mixed micelles between EO and CTAB. Curve 3 of Figure 1 is typical of suspension of bath type 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 concentration far below the critical micelle concentration(CMC) for surfactant homomicelles by aqueous solution of EO and CTAB.

Raman Spectra of EO on Interaction with CTAB

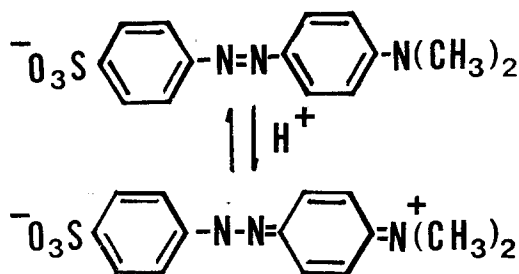


Chart 1: Structure of EO.

Raman spectra are shown Figures 2 and 3 to observe the structure change of dye which interacts with CTAB.

The deep-yellowish color of EO in a neutral or a basic solution changes to reddish color when the solution is acidified to pH below the color-change interval of EO. This color change has been attributed to a change of the molecular structure from an azo-type in the basic solution to a quinoid type in the acidic solution with the protonation to azo group as shown in Chart 1.

Curves 1 and 2 of Figure 2 show the marked spectra difference occurring in such a structure change.

In spectra of EO in water the doublet peaks at 1400 and 1436 Cm^{-1} are assigned to azo group modes, N=N symmetrical stretching ($\nu_{N=N}$). The peak at 1162 Cm^{-1} is assigned to a phenyl-N stretching vibration of the azo group. The frequencies of other peaks are summarized in Table I together with their assignments.¹¹⁻¹³⁾

EO is in the trans azo conformation and there is no twisting of the phenyl groups (cis-form) from their aqueous conformation as indicated by the peaks at 1400 and 1436 Cm^{-1} . Twisting of the phenyl rings would be

expected to produce a large increase in frequency of one of the bands because the position of the N=N vibration will depend strongly on the degree of conjugation of the electrons and this will, in turn, be seriously affected by such twisting. The presence of the cis form would have produced a shift of nearly 100 Cm^{-1} and given the stretching frequency around 1500 Cm^{-1} .¹⁴⁾

Curve 2 of Figure 2 represents the resonance Raman spectrum of EO in acidic solution.

The acidic form shows no strong Raman peaks assignable to the N=N stretching vibration near 1400 and 1436 Cm^{-1} . A strong peak at 1639 Cm^{-1} is assigned to a stretching vibration of the ring C=C bond of the quinoid type.

The intensity of this peak is weaker than that of the characteristic peaks of azo type. Since 488.0nm excitation used in the resonance Raman spectra is more sensitive to azo type at 475nm than quinoid type of which absorption maximum occurs at 510nm.⁹⁾ A peak at 1621 Cm^{-1} is assigned to C=N stretching vibration and a peak due to N-N stretching vibration is observed at 1204 Cm^{-1} . Assignments of other peaks of quinoid type are reported in Table II.

Curve 3 of Figure 2 shows the Raman bands of EO on interaction with CTAB.

It is observed that main peaks in curve 3 appear almost at the same position as those in curve 1 except near 1162 and 1618 Cm^{-1} . Only the spectra change near 1162 and 1618 Cm^{-1} may be caused by no change of a skeletal structure of EO itself, but by the environment change of EO.

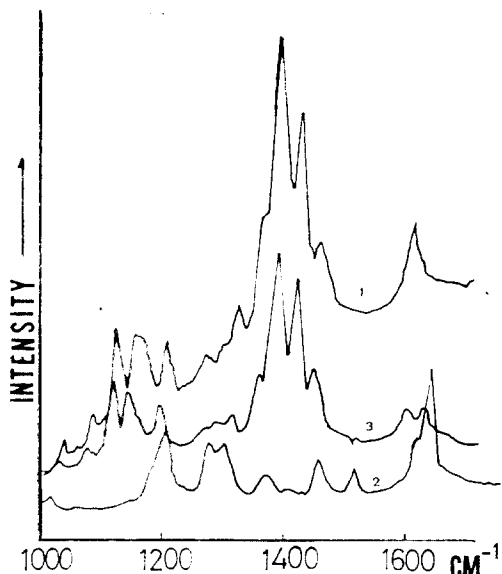


Fig. 2: Resonance Raman spectra of 3×10^{-5} M EO, 488.0 nm.

- 1) in water.
- 2) in 1.94 M HCl.
- 3) in 5×10^{-4} M CTAB.

Table I: Observed frequencies and assignments for the basic form of EO.

Frequency (Cm^{-1})	Assignment
1162 m	Phenyl-N str.
1213 m	Benzene ring
1328 w	Benzene ring
1370 s	C-N str.
1400 vs	N=N str.
1436 vs	N=N str.
1463 m	Benzene ring
1618 m	Benzene ring

The molecular structure of EO bound to CTAB is entirely different from that of the acidic form of EO and from that of the cis azo type. As judged by these it is suggested that EO retain its trans azo type on interaction with CTAB no such a conformational change.

Table II: Observed frequencies and assignments for the acidic form of EO.

Frequency (Cm^{-1})	Assignment
1204 s	N-N str.
1294 s	Ph-M str.
1367 w	C-C str.
1456 m	Benzene ring
1515 m	Benzene ring
1621 s	C=N str.
1639 vs	C=C str.

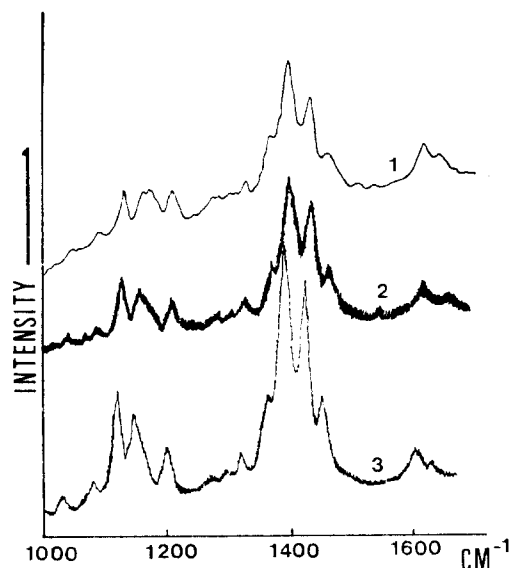


Fig. 3: Resonance Raman spectra of 3×10^{-5} M EO, 488.0 nm.

- 1) in 2×10^{-5} M CTAB + 1×10^{-4} M K_2SO_4 , λ_{max} 475nm.
- 2) in 6×10^{-5} M CTAB + 1×10^{-4} M K_2SO_4 , λ_{max} 395nm.
- 3) in 2×10^{-4} M CTAB + 3×10^{-4} M K_2SO_4 , λ_{max} 410nm.

An irradiation experiment of analogue, MO also showed the same results.⁸⁾

Accordingly, the twisting around the N=N bond can not be the reason why the absorption maximum shifts from 475 to 395nm.

In Figure 3 the Raman spectra in various absorption maxima on adding CTAB and salts are recorded.

The Raman spectrum in occurring absorption peak at 475nm is very similar to that of EO itself. It is observed that the Raman spectrum in an absorption peak at 395nm is unstably recorded and its intensity in an absorption peak with a maximum near 410nm is increased. About these, the precise investigation will be carried out.

Effect of Salts on C.M.C. for the Mixed Micelle

The typical data of the effect of added salts on the absorption maxima are shown in Figure 4.

In the absence of added salt an aqueous solution of EO ($3 \times 10^{-5} \text{M}$) and CTAB ($2 \times 10^{-4} \text{M}$) has an absorption maximum at 395nm.

When $2 \times 10^{-3} \text{M}$ KCl or K_2SO_4 is added in an aqueous solution of EO and CTAB, the absorption maximum shifts to 402 or 429nm, respectively. The red shifts of the absorption maximum in the presence of salts are identical with the changes obtained by increasing the surfactant concentration in no added salts.

There is also a progressive increase in absorptivity with increasing the concentration of salt.

Accordingly salts promote the spectral shift of absorption maximum and decrease critical micelle concentration (c.m.c.) for the mixed micelle as well as CMC for surfactant homomicelles.

At c.m.c. of CTAB for the mixed micelle and absorption band with a maximum at

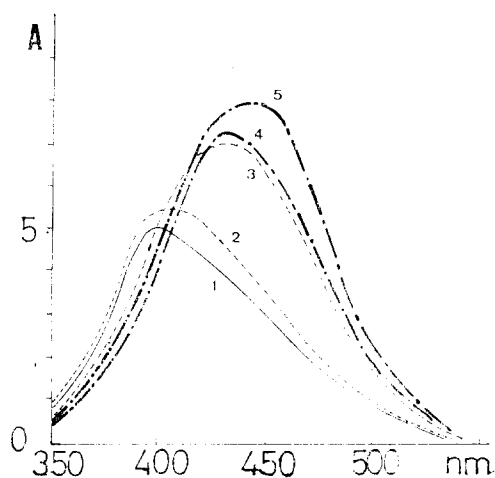


Fig. 4: Absorption spectra of EO in the presence of CTAB for different addition of salts.

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

CTAB conc.: $2 \times 10^{-4} \text{M}$

salt conc. : 1) 0, 2) $2 \times 10^{-3} \text{M}$ KCl, 3) $2 \times 10^{-3} \text{M}$ K_2SO_4 , 4) $1 \times 10^{-1} \text{M}$ KCl, 5) $1 \times 10^{-1} \text{M}$ K_2SO_4

395nm is found. The c.m.c. for the mixed micelle is far below the CMC for surfactant homomicelle.

It was reported that the CMC for CTAB homomicelle is $9.2 \times 10^{-4} \text{M}$ at 25°C .¹⁷⁾ By our study the c.m.c. of CTAB for the mixed micelle is $2 \times 10^{-4} \text{M}$ in $3 \times 10^{-5} \text{M}$ EO and no added salts.

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 homomicelles.¹⁸⁾

At adding salts the absorption maxima at

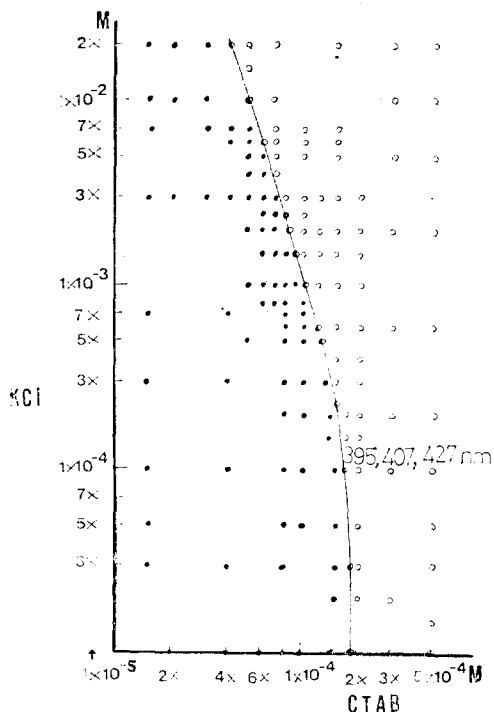


Fig. 5: Log-log plot of the change of c.m.c. for CTAB in EO ($3 \times 10^{-5} \text{M}$) and added KCl resulting from λ_{max} . Open data points for λ_{max} in blue-shift; Filled data points for λ_{max} in red-shift.

various concentration of CTAB shift to lower wavelengths and in turn, to higher wavelengths. In Figure 5 the absorption maxima in blue shifts are represented by open data points and those in red shifts by filled data points. And the c.m.c.s of CTAB with an absorption maximum at 395nm in the presence of various amounts of KCl are recorded.

Increasing concentration of KCl the c.m.c. for mixed micelle gradually decreased. In $1 \times 10^{-4} \text{M}$ KCl solution the absorption maxima show 397, 407, and 427 nm,

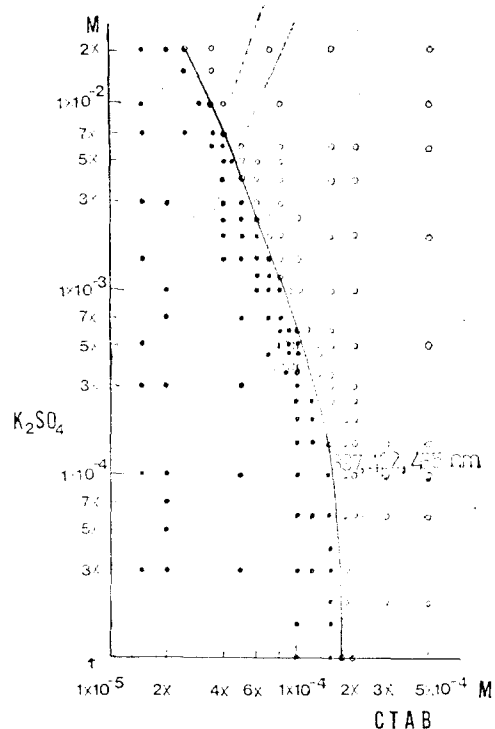


Fig. 6: Log-log plot of the change of c.m.c. for CTAB in EO ($3 \times 10^{-5} \text{M}$) and added K_2SO_4 resulting from λ_{max} . Open data points for λ_{max} in blue-shift; Filled data points for λ_{max} in red-shift.

respectively, at concentration of CTAB, 2×10^{-4} , 3×10^{-4} , and $5 \times 10^{-4} \text{M}$ above c.m.c. for the mixed micelle.

Figure 6 shows the analogous phenomenon in K_2SO_4 solution. The c.m.c. is depressed with added K_2SO_4 and in $1 \times 10^{-4} \text{M}$ K_2SO_4 solution the absorption maxima show 397, 422, and 435nm at concentration of CTAB, 1.8×10^{-4} , 3×10^{-4} , and $5 \times 10^{-4} \text{M}$, respectively.

In order to easily compare c.m.c.s in added salts, it is convenient to plot together changes of c.m.c.s in the presence of KCl or K_2SO_4 . Such plots are given in Figure 7.

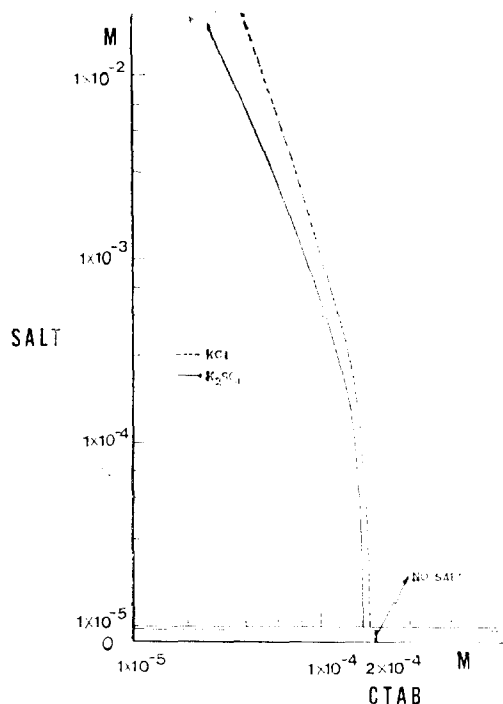


Fig. 7: Log-log plot of the change of c.m.c. for CTAB.

In case of no added salt, the c.m.c. for the mixed micelle is 2×10^{-4} M. As increasing the salt concentration the c.m.c.s are depressed and divalent salt, K_2SO_4 has an effect on c.m.c. and spectral shift more than monovalent, KCl does.

Some representative c.m.c.s of CTAB in added salt and salt concentrations at then are summarized in Tables III and IV.

At surfactant:dye (S:D) ratio of 6.7 the mixed micelle is formed in the absence of added salt. On adding salt, a competition between counterions and anionic head groups of dye for the cationic head groups has the mixed micelles formed at lower S:D ratio

The c.m.c.s obtained in added salt are in-

Table III: The c. m. c. of CTAB for the mixed micelle in the presence of KCl at 25°C. (EO 3×10^{-5} M)

Conc. of KCl (M)	c.m.c. (M)	S/D ($\frac{\text{c.m.c. of CTAB}}{\text{conc. of EO}}$)
0	$x \times 10^{-4}$	6.7
3×10^{-5}	1.8×10^{-4}	6
2.3×10^{-4}	1.5×10^{-4}	5
6×10^{-4}	1.2×10^{-4}	4
1×10^{-3}	1×10^{-4}	3.3
2×10^{-3}	8×10^{-5}	2.7
6×10^{-3}	6×10^{-5}	2
1×10^{-2}	5×10^{-5}	1.7
2×10^{-2}	4×10^{-5}	1.3

Table IV: The c. m. c. of CTAB for the mixed micelle in the presence of K_2SO_4 at 25°C. (EO 3×10^{-5} M).

Conc. of K_2SO_4 (M)	c.m.c. (M)	S/D ($\frac{\text{c.m.c. of CTAB}}{\text{conc. of EO}}$)
0	2×10^{-4}	6.7
1×10^{-5}	1.7×10^{-4}	6.7
1.5×10^{-4}	1.5×10^{-4}	5
6×10^{-4}	1×10^{-4}	3.3
1.2×10^{-3}	8×10^{-5}	2.7
2.5×10^{-3}	6×10^{-5}	2
7×10^{-3}	4×10^{-5}	1.3
2×10^{-2}	2.5×10^{-5}	0.83

trodded in equation of Corrin & Harkins.¹⁹⁾

The effect of the concentration of salt is given by the following equation

$$\text{KCl}; \log C_0 = -0.33 \log (C_0 + C_\alpha) - 4.96$$

$$\text{K}_2\text{SO}_4; \log C_0 = -0.41 \log (C_0 + C_\alpha) - 5.29$$

where C_0 is the c.m.c. of CTAB for the mixed micelle and C_α is the concentration of added salt in moles per liter.

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

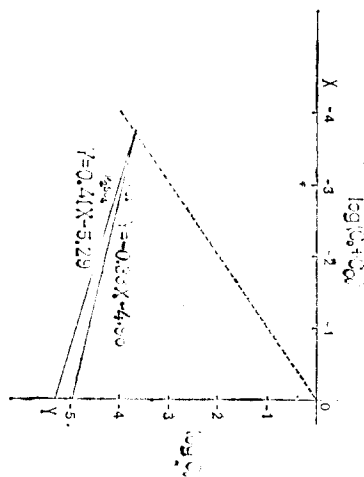


Fig. 8: Plots of $\log (C_0 + C_a)$ versus $\log C_0$.
 C_0 : critical micelle conc. of CTAB.
 C_a : co nc. of added salt.

In Figure 8 $\log (C_0 + C_a)$ in X-axis is plotted against $\log C_0$ in Y-axis.

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 reserchers.^{19~21)} For non-ionics and zwitterionics the preceding relationship does not hold.^{22,23)} Instead, the effect of salt is given by the equation

$$\log C_0 = -K C_a + \text{Constant}, \quad (C_a < 1)$$

where K is a constant for a particular surfactant, electrolyte and temperature.

This is to be expected that the mixed micelle is charged positively, though less charged than surfactant homomicelle due to neutralizing cationic head groups by anionic head groups of dye.

The higher surfactant concentration is the more similarly the characteristic of the mixed micelle changes to that of surfactant

homomicelle and monomeric dye solubilized in CTAB micelle consisting mainly of surfactant. An absorption maximum of this dye is near 460nm, which is not investigated precisely by the author however may be characteristic of EO in a nonaqueous micro-environment.

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