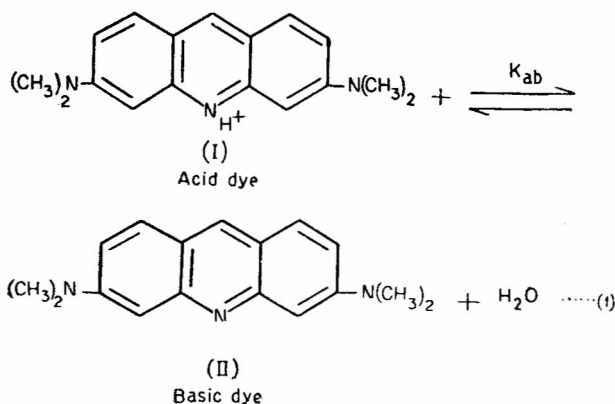Fig. 1 — Effect of pH on the spectra of acridine orange at $1 \cdot 46 \times 10^{-5} M$ [Curves 1 and 2: pH = 9·19 and 9·81; curve 3: excess acid; curves 4-11: pH = 9·97, 10·11, 10·25, 10·58, 10·61, 10·80, 11·22 and 11·47]

(I)
Acid dye

(II)
Basic dye

evaluated using Eq. 2 applied earlier to similar systems[5,6]:

$$\frac{[C_a]}{A} = \frac{1}{\epsilon_b} + \frac{1}{K_{ab}\epsilon_b[OH^-]} \qquad ...(2)$$

where $[C_a]$ is the fixed acid dye concentration, A is the absorbance of the dye base at 430 nm; when the concentration of the added base is $[OH^-]$, ϵ_b is the molar extinction of the dye base and K_{ab} is the equilibrium constant.

In view of the very low concentrations of the dye ($\sim 10^{-5}M$) as well as that of the base ($\sim 10^{-4}M$) used in solutions, their activities are taken as equal to their concentrations. The plot of $[C_a]/A$ against $1/[OH^-]$ at 25° has been found to be linear, the least-square analysis of the data yielded K_{ab} and ϵ_b as $(3 \cdot 19 \pm 0 \cdot 21) \times 10^4$ litre mole^{-1} and $(2 \cdot 02 \pm 0 \cdot 27) \times 10^4$ litre mole^{-1} cm^{-1} respectively. The value of ϵ_b agrees well with that obtained from Beer's law $[(1 \cdot 95 \pm 0 \cdot 05) \times 10^4$ litre mole^{-1} cm$^{-1}]$.

Among other effects of pH on the dye, it has been observed that a pH>11·5 is required for the complete conversion of AOHCl to its conjugate base, AO. For such a conversion[4], a similar dye, trimethylthionine (TMT) needs a pH of 12·2. On the other hand, the other closely similar dye, methylene blue, gets demethylated in basic environ-

ment producing TMT which can be extracted with benzene. Our experience with acridine orange is that so long as the pH is >7, partition of the basic dye (yellow with greenish fluorescence) between benzene and water is unidirectional towards the benzene phase. Repeated shaking with fresh water under atmospheric condition can ultimately bring the dye into the aqueous phase, and in course of this procedure the dye turns into the acid form. However, addition of a non-polar solvent like dioxane (which mixes with both benzene and water) helps in distributing the basic dye molecules into both the phases. The solid mass obtained from the benzene extract when redissolved in water, exhibits spectra identical with that of the acid dye. The great instability of AO in its basic form is thus explained. Unlike methylene blue, acridine orange does not get demethylated in basic environment.

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Interaction of Cationic Surfactants with Polytungstate

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The interaction of cationic surfactants, viz. cetyl-pyridinium bromide, dodecylpyridinium bromide and cetyltrimethylammonium bromide with polytungstate has been studied at pH 4·0 and 6·6. When the reactants are mixed in equivalent amounts, the solid interaction products separate out, the analysis of which gives the ratio 1 : 6 (polytungstate-surfactant) thereby conforming the existence of metatungstate anion. This ratio has been further confirmed by interfacial tension studies of surfactant and polytungstate mixtures. However, when one of the reactants is present in excess, the product goes into colloidal state and the charge of the sol depends on the reactant present in excess.

IN a recent communication[1] we have reported our results on the interaction of polyvandate and polymolybdate with cationic surfactants. The present note reports results on the interaction of cetyl-pyridinium bromide (CPB), dodecylpyridinium bromide (DPB) and cetyltrimethylammonium bromide (CTMAB) with polytungstate at different pH values.

The solutions of cationic surfactants (BDH), and sodium tungstate were made in doubly distilled water and pH adjusted with dil. HCl and NaOH.

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At pH 4, the predominating polyanionic species[2,3] existing is the metatungstate ion, $(H_2W_{12}O_{40})^{6-}$. When to a solution of polytungstate of pH 4, an equivalent amount of a cationic surfactant was added slowly, a white product precipitated out. In this way with CPB, DPB and CTMAB, three products were obtained, the analyses of which are given below:

Formula	Found (%) (Calc.)		
	C	H	N
CPB+polytungstate			
$(C_{21}H_{38}N)_6(H_2W_{12}O_{40})$	32·33	4·88	1·59
	(32·17)	(4·84)	(1·78)
DPB+polytungstate			
$(C_{17}H_{30}N)_6(H_2W_{12}O_{40})$	28·99	4·18	1·74
	(28·29)	(4·17)	(1·92)
CTMAB+polytungstate			
$(C_{19}H_{42}N)_6(H_2W_{12}O_{40})$	29·74	5·58	1·70
	(29·66)	(5·54)	(1·83)

The interaction is obviously electrostatic and interaction ratio is 1:6 for polytungstate anion to surfactant cation. Our results, therefore, confirm the existence of metatungstate anion. If other polyanionic species[1] are present, they do not react with surfactants to yield insoluble products. It is possible that they may change into metatungstate anion as the product starts precipitating out.

In presence of excess of either of the reagent, the interaction product goes into colloidal state. In the presence of excess of tungstate the interaction product was peptized due to the adsorption of metatungstate anions (which are present in excess) yielding a white negatively charged sol. Zeta potential of the sol was found to be 48 and 36 mV for metatungstate sol with CTMAB and CPB, respectively. Sodium ions were found to be counter ions.

Where surfactant and polytungstate are almost in equal amounts, the interaction product settles down and no sol formation was observed. In the presence of excess of surfactant, the product got dispersed to yield positively charged sol due to the adsorption of surfactant cation on the interaction product. The counter ions in the sol were found to be chloride ions.

The adsorption of surfactant cations as well as the interaction ratio were further investigated by interfacial tension studies. The surface tension of the polytungstate-surfactant mixtures was measured 24 hr after mixing with the help of a torsion balance and the plots between surface tension and cationic surfactant concentration were obtained (Fig. 1). The initial region, where there is very small decrease in surface tension, corresponds to the formation of negatively charged sol. However, at point D of the curves, the interaction product settled down indicating there that all the metatungstate anion has reacted with surfactant. Just above point D, the added surfactant is in excess and the excess amount of it lowers the surface tension drastically[4]. Therefore, the region DE, corresponded to the region where the interaction product had settled down and a small amount of free surfactant was present. Obviously, the point D must correspond to equi-
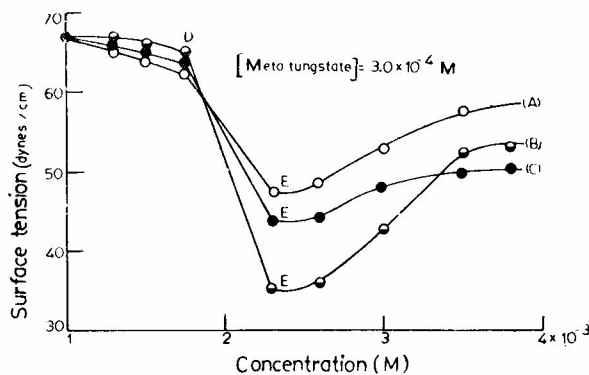

Fig. 1 — Plots between surface tension and concentration of the surfactants [Conc. of metatungstate$=3\cdot0\times10^{-4}M$; surfactants used: (A) CPB; (B) DPB; and (C) CTMAB]

valence point and from it, the interaction ratio is found to be 1:6 for metatungstate anion to surfactant cation. As we go beyond point E, further addition of surfactant dispersed the interaction product to yield positively charged sol due to the adsorption of surfactant cations. This removal of surfactant cations from solution due to adsorption causes the surface tension to increase.

At pH 6·6, the polyanionic species[1,5] reported to exist is protonated hexatungstate $[HW_6O_{21}]^{5-}$ anion. The addition of equivalent amounts of surfactant to polytungstate at pH 6·6 yielded white interaction products, which were isolated and analysed. The results are given below:

Formula	Found (%) (Calc.)		
	C	H	N
CPB+polytungstate			
$(C_{21}H_{38}N)_4(H_2W_6O_{21}).5H_2O$	36·16	5·72	1·75
	(36·46)	(5·93)	(2·22)
DPB+polytungstate			
$(C_{17}H_{36}N)_4(H_2W_6O_{21}).5H_2O$	32·73	5·35	2·21
	(32·16)	(5·20)	(2·20)
CTMAB+polytungstate			
$(C_{19}H_{42}N)_4(H_2W_6O_{21}).5H_2O$	34·25	6·64	2·15
	(34·01)	(6·71)	(2·08)

The presence of 5 molecules of water was also confirmed by weight loss study. The above results confirm the existence of diprotonated hexatungstate anion $(H_2W_6O_{21})^{4-}$ instead of monoprotonated anion at pH 6 6. In this case also, negatively charged sol was formed in the presence of excess of hexatungstate anion and positively charged sol in presence of excess of surfactant cation. The surface tension vs surfactant concentration plots of hexatungstate-surfactant mixtures were similar to those given in Fig. 1. The plots indicated an interaction ratio of 1:4 for hexatungstate anion to surfactant cation.

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