

Fig. 1 — Dependence of true dissolution potential on temperature

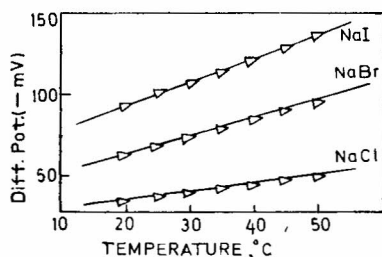


Fig. 2 — Dependence of diffusion potential on temperature

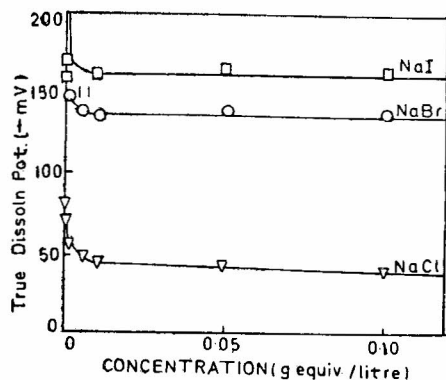


Fig. 3 — Plots of true dissolution potential versus concentration of electrolyte

where constants  $A$  and  $B$  are given by

$$\frac{RT}{F} \left( \frac{u_+ - u_-}{u_+ + u_-} \right) \ln C_1 \text{ and } \frac{RT}{F} \left( \frac{u_+ - u_-}{u_+ + u_-} \right)$$

respectively and  $C_2$  is the concentration of the electrolytic solution in the cell. This leads to a linear relationship of diffusion potential with  $\log C_2$ . Further, it is noteworthy that the intrapolation of the curve to zero diffusion potential meets the saturation point. This is obvious because the process of diffusion ceases when both the diffusing solutions of the same electrolyte are saturated, i.e. the same concentration.

The observed dissolution potential has been found to decrease exponentially with concentration. This is in agreement with the observation of Rastogi *et al.*<sup>3</sup>. However, the true dissolution potential does

not decrease exponentially with concentration (Fig. 3) but the data fit the following empirical relations:

$$(\text{True dissoln pot.})_{\text{NaCl}} = 3e^{-461C} - 40C + 44$$

$$(\text{True dissoln pot.})_{\text{NaBr}} = 22e^{-1277C} - 40C + 142$$

$$(\text{True dissoln pot.})_{\text{NaI}} = 104e^{-3329C} - 18C + 164$$

It can be seen from Figs. 1 and 2 that true dissolution potential decreases and the diffusion potential increases linearly with increasing temperature. The linearity of diffusion potential is in accordance with Eq. (1)

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#### pH Effect on Acridine Orange Dye

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The basic and the acid forms of acridine orange dye interchange in the pH range 10.0–11.5 yielding an equilibrium constant  $(3.19 \pm 0.21) \times 10^4$  litre mole<sup>-1</sup> at 25°. The dye base is very unstable, and unlike methylene blue, it undergoes no demethylation in basic environment.

DETAILED physico-chemical properties of acridine orange dye have been presented recently<sup>1,2</sup>. It has been reported that in a close pH range (10.0–11.5) the basic and acid forms of the dye undergo a remarkable visible spectral interchange through a sharp isosbestic point at 445 nm. Although physico-chemical properties of dyes in acidic and basic environments reveal interesting features<sup>3,4</sup>, such a conspicuous acid-base conversion phenomenon (Fig. 1) has not been reported on dye systems. In this note the quantitative aspect of this conversion phenomenon together with some other effects of pH are reported. No systematic study of acridine orange dye (AO) at higher pH was made in the past.

The equilibrium constant of the acid-base conversion (represented by Eq. 1) process has been

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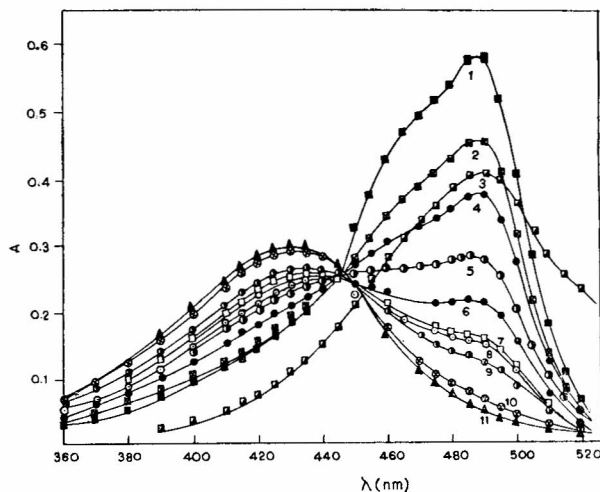
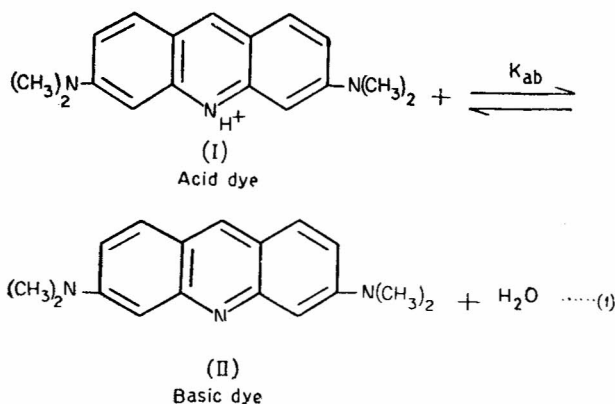


Fig. 1 — Effect of  $pH$  on the spectra of acridine orange at  $1.46 \times 10^{-5}M$  [Curves 1 and 2:  $pH = 9.19$  and  $9.81$ ; curve 3: excess acid; curves 4-11:  $pH = 9.97, 10.11, 10.25, 10.58, 10.61, 10.80, 11.22$  and  $11.47$ ]



evaluated using Eq. 2 applied earlier to similar systems<sup>5,6</sup>:

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

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  $[OH^-]$ ,  $\epsilon_b$  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  $25^\circ$  has been found to be linear, the least-square analysis of the data yielded  $K_{ab}$  and  $\epsilon_b$  as  $(3.19 \pm 0.21) \times 10^4$  litre mole<sup>-1</sup> and  $(2.02 \pm 0.27) \times 10^4$  litre mole<sup>-1</sup> cm<sup>-1</sup> respectively. The value of  $\epsilon_b$  agrees well with that obtained from Beer's law  $[(1.95 \pm 0.05) \times 10^4$  litre mole<sup>-1</sup> cm<sup>-1</sup>].

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<sup>4</sup>, 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. cetylpyridinium 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<sup>1</sup> we have reported our results on the interaction of polyvanadate and polymolybdate with cationic surfactants. The present note reports results on the interaction of cetylpyridinium 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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