Association Constant of Crystal Violet in Micellar Aggregates: Determination by Spectroscopic Techniques†

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The effects upon the absorption spectrum of Crystal Violet (CV) were used to determine the association constant of CV with different micellar aggregates.

Crystal Violet (CV) is a carbonium ion that is stabilised by the presence of aromatic rings, which endow it with strong resonance that results in a deep blue–violet colour with an absorption maximum in the visible region ($\lambda_{max} = 590$ nm).[1] The reactivity of this cation is of great physicochemical interest since it was used together with those of similar cations for establishing Ritchie's N^+ nucleophilic index.[2] Its reactivity towards the OH^- ion has been especially widely studied in aqueous solutions[3] and other media.[4]

In this paper the association constants of CV with micelles formed by lauryl(trimethyl)ammonium bromide (LTABr), cetyl(trimethyl)ammonium bromide (CTABr), cetyl(trimethyl)ammonium chloride (CTACl), tetramethyl(trimethyl)ammonium bromide (TTABr), octadecyl(trimethyl)ammonium bromide (OTABr), cetyl pyridinium chloride (CCP), dodecylpyridinium chloride (CDP) and sodium dodecyl sulfate (SDS) have been evaluated by means of spectroscopy.

Experimental

All chemicals used were of the highest commercially available purity and none required further purification. The experimental procedure employed has been described in detail elsewhere.[5]

Results and Discussion

The association constant of CV to micellar aggregates was determined spectrophotometrically using reported procedures.[5] Mixtures containing variable concentrations of different micellar surfactants and constant amounts of CV were thermostatted at 25 °C and their spectra recorded against a suitable reference. The association constant was obtained from eqn. (1).

$$A = \frac{A_w + A_m K_{CV} D_n}{1 + K_{CV} D_n} \qquad [1]$$

which can be linearised to eqn. (2)

$$\frac{A - A_w}{A_m - A} = K_{CV} D_n \qquad [2]$$

where K_{CV} is the association constant of CV with the micelles, and D_n is the concentration of micellised surfactant ([surfactant] − cmc); the cmc values were measured by conductivity methods.[6] Absorbance values were measured at 590 nm, A_w being the absorbance of CV in pure water, A that in the presence of micelles, and A_m the limiting absorbance (*viz.* that measured when all CV had been

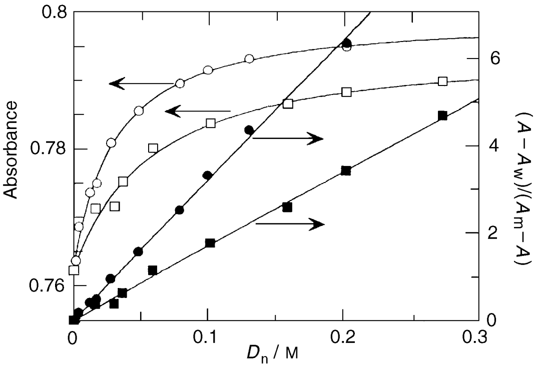

Fig. 1 Fitting of the absorbance values to eqn. (1) (open symbols) and eqn. (2) (closed symbols): ■ and □, LTABr micelles; ● and ○, TTABr micelles. The solid lines correspond with the fits to eqns. (1) and (2), respectively

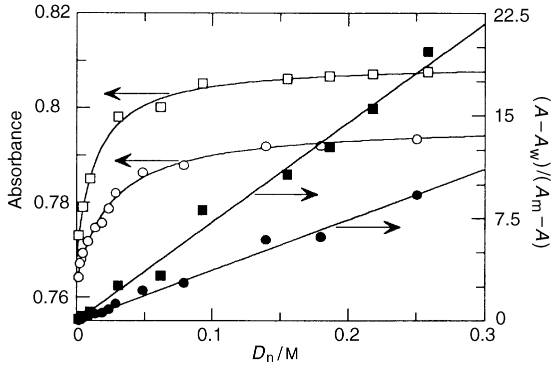

Fig. 2 Fitting of the absorbance values to eqn. (1) (open ymbols) and eqn. (2) (closed symbols): ■ and □, OTACl micelles; ● and ○, CTACl micelles. The solid lines correspond with the fits to eqns. (1) and (2), respectively

Table 1 K_{CV} values obtained for different surfactants

Surfactant	Chain length	CMC/M	K_{CV}
SDS	12	8.10×10^{-3}	25.0 ± 1.2
LTABr	12	1.25×10^{-2}	17.0 ± 0.2
TTABr	14	3.50×10^{-3}	32.1 ± 0.3
CTABr	16	1.48×10^{-3}	37.2 ± 0.9
CTACl	16	1.50×10^{-3}	37.1 ± 0.8
OTACl	18	5.00×10^{-5}	42.3 ± 0.9
CDP	12	1.50×10^{-3}	15.4 ± 0.3
CCP	16	5.20×10^{-4}	37.4 ± 1.3

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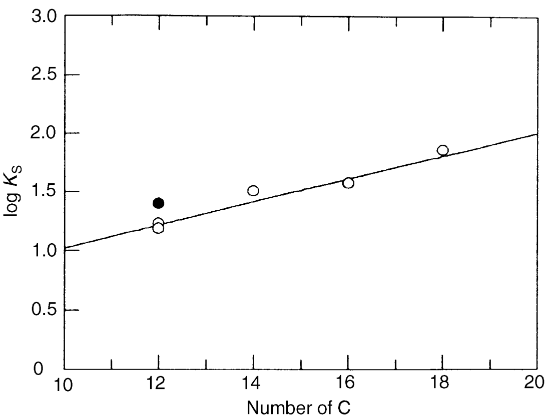

Fig. 3 Variation of log K_s with the surfactant chain length: (○) cationic surfactants, (●) anionic surfactants

incorporated into the micellar pseudophase; in our case the A_m values were obtained by the fit of eqn. (1) to the experimental data). As can be seen in Fig. 1 and Fig. 2, the eqns. (1) and (2) fitted the results well. The values obtained in this way are shown in Table 1.

It is well known that the CV occurs as two helicoidal isomers[1] owing to the strong steric hindrance between the benzene *ortho* protons which lead to a non-planar configuration. The presence of these two isomers gives rise to two different absorption bands in the visible spectrum at 590 and 540 nm.[1] The ratio between these two bands, which is proportional to the relative population of the two isomers, stays constant under the experimental conditions (1.48) and equal to the value in water.[7]

From the K_{CV} values we can confirm that the main driving force for the association of organic substrates to micellar aggregates is the different polarity between pure water and micellar media. In fact, the value of K_{CV} increases with the length of the surfactant chain (Fig. 3). From these results, we can conclude that neither the nature of head group (ammonium salt head group and pyridinium head group have no influence upon K_{CV}: CTABr, CTACl and CCP have the same K_{CV} value (37.2, 37.1 and 37.4 respectively) nor does the nature of the micellar counterion [CTABr and CTACl have the same K_{CV} value (37.2, 37.1 respectively)] have any noticeable influence upon the association of CV to the micellar phase.

The SDS value is slightly larger than that for CDP and LTABr. This difference is due to the different head group charge. The differences observed between SDS–CDP and SDS–LTABr can be explained from the electrostatic interaction between CV (positively charged) and CDP and LTABr (cationic surfactants) as compared with SDS (anionic surfactant).

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