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The aggregation of chlorhexidine digluconate in aqueous solution from optical rotatory dispersion measurements

In our continuing investigations of the optical rotatory dispersion (ORD) and circular dichroism (CD) of optically active surfactants and the possible detection of micelle or aggregate formation by this technique (Bonkoski & Perrin, 1968, 1969; Mukerjee, Perrin & Witzke, 1970), we have for the first time investigated a system in which the optical activity is centred in the counterion rather than the core of the aggregate. The chlorhexidine digluconate solutions chosen for these studies were prepared from the recrystallized base (Ayerst Labs., Inc., Rouses Point, N.Y.) and the theoretical amount of 1,5-gluconolactone in de-ionized water. Heard & Ashworth (1968) have reported a CMC of $6{\cdot}6 \times 10^{-3}$M for chlorhexidine digluconate, but lower values could be extrapolated from their surface tension and conductance data. We have found, using a Beckman Model RC 16B2 conductivity bridge (Beckman Instruments, Cedar Grove, New Jersey), a CMC of approximately $4{\cdot}4 \times 10^{-3}$M at $25{\cdot}0 \pm 0{\cdot}01°$ (Fig. 1A). This value is in good agreement with the value obtained from optical rotatory dispersion measurements (Fig. 1B and 2). In the ORD investigations

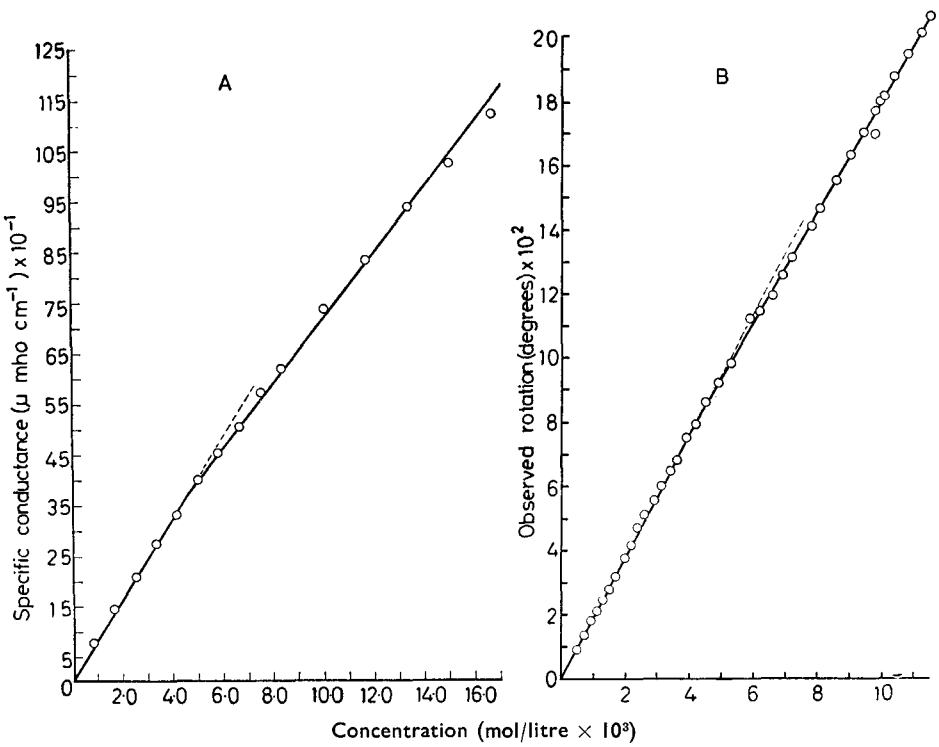

Fig. 1.A. Specific conductances of chlorhexidine digluconate in de-ionized water at 25°. B. Observed rotations at 317·5 nm for chlorhexidine digluconate solutions at 25°.

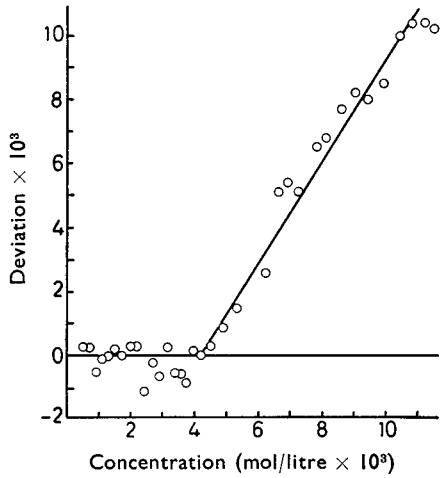

Fig. 2. Deviation plot of the data from Fig. 1B. Deviation being defined as observed rotation divided by (19·04 × concentration).

(Cary Model 60, Cary Instruments, Monrovia, California) at 25·0 ± 0·1° in 5 cm cells, the solutions were scanned from 400 down to 310 nm, where the absorption of the stronger solutions was too great for accurate quantitative analysis. Over this wavelength range the solutions gave apparently plain dispersion curves. Observed rotation for various concentrations of surfactant at 317·5 nm is shown in Fig. 1B, the real but small break at the CMC is emphasized by the deviation plot of Fig. 2. Analysis of the apparently plain curves by a single-term Drude equation (Drude, 1906), as was performed for the octyl glucoside (Mukerjee & others, 1970), proved unsuccessful; apparently more than one electronic transition is responsible for the gluconate curves. The change in rotation found after micelle formation is probably related to the change in ionization of the gluconate on aggregation; however, the dangers of mutorotation in extremes of pH make confirmation of this difficult. It should be noted that the rotations of the gluconate solutions had not changed 48 h after the experimental determinations.

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