Surface tension measurements yielded critical micelle concentrations (cmcs) for the mixtures which were significantly lower than the accepted values for the pure compounds, because of attraction between the head groups in the mixed micelles. NaC with TTAB formed homogenous solutions in all mixing proportions. Light scattering results (turbidity *vs* mole ratio) yielded a sharp maximum at a ratio of 1:1. Debye plots gave micelle molecular weights (M.M.W.) for the mixed micelles (Table). Intrinsic viscosities, [η], suggested approximately spherical micelles, with complete suppression of the electroviscous effect in 1:1 molar solutions.

Mixtures of NaDC with TTAB separated into two liquid phases (coacervation) at close to 1:1 molar ratios. Light scattering and viscosity measurements indicated large, non-spherical micelles close to the phase-separation point, caused by small quasi-spherical micelles aggregating. Estimates of hydration for various axial ratios indicated that pure bile salt micelles had an axial ratio of approximately 3:1 in 0·15 M NaBr solution, whereas micelles formed from equimolar amount of NaC and TTAB were approximately spherical. Consideration of molecular dimensions, combined with the models proposed by Small (1971) for bile salt micelles support these conclusions.

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Substituted ethoxy groups in anionic surfactants; effect on cmc, area per molecule and micellar counterion binding

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Anionic surfactants of the type $CH_3(CH_2)_n$–$(OC_2H_4)_X$ SO_4^- Na^+ were synthesized and the effect of ethoxy group number on surfactant properties as measured by conductivity, surface tension and sodium ion activity were determined. Results are summarized in the Table where C_n refers to hydrocarbon chain length and E_x to ethoxy group number.

Surfactant	cmc mol^{-1} × 10^3 conductance	surface tension	Na ion activity	area per molecule Å^2	α
$C_{12}E_0$	8·1	7·9	8·0	68	0·21
$C_{12}E_1$	4·5	4·3	4·2	80	0·29
$C_{12}E_2$	2·8	2·7	2·8	110	0·36
$C_{10}E_2$	12	12	12	101	0·42
$C_{14}E_2$	0·85	0·80	0·82	116	0·30
$C_{16}E_2$	0·22	—	0·20	—	—

The surface area occupied by each surfactant was obtained from the Gibbs equation and the sodium ion activities were measured using a glass sodium ion responsive electrode. The degree of dissociation, α, was obtained from a plot of activity coefficient against concn^{-1} (Ingram & Jones, 1969).

As the ethoxy group number increased the cmc decreased even though the surfactants became more polar and water soluble. This decrease related to the increased molecular cross sectional area and degree of dissociation. It was assumed that the hydrated ethoxy groups sterically prevented close contact between neighbouring ionic head groups. Since the surface micellar change density was reduced, the degree of dissociation increased (reduction in counterion binding). As the hydrocarbon chain length increased, the cmc and the degree of dissociation decreased because micelles became more compact due to increased van der Waals attraction forces.

Plots of log cmc against ethoxy groups or hydrocarbon chain length were linear but with different slopes. Although increased hydrocarbon chain length or ethoxy group number decreased the cmc, the effect on counterion binding was different indicating that the mechanisms involved were dissimilar.

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pH–Mobility plots for drug suspension systems and the effect of added surface active agents

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The effect of various surface active agents (SAA), both alone and as mixed ionic types, on the zeta potential of a model suspension system has been previously reported (Kayes, 1973).

An attempt has been made to apply these results to drug suspension systems of griseofulvin, nalidixic acid, thiabendazole and betamethasone. The mobilities of the suspension particles were measured using the flat cell assembly of the Rank Mark II Particle Microelectrophoresis apparatus. The pH-mobility curves, together with the chemical structure of the four drugs are shown below.

With griseofulvin the positive charge at low pH can be attributed in part to protonation of the $\alpha\beta$-unsaturated ketone and partly to the adsorption of hydrogen ions; the negative charge at higher pH, to adsorption of hydroxyl ions.

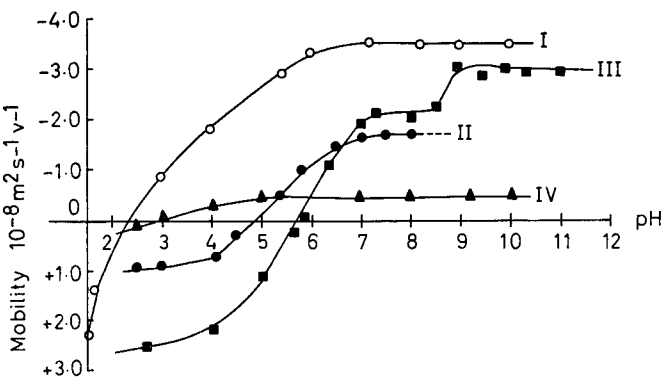
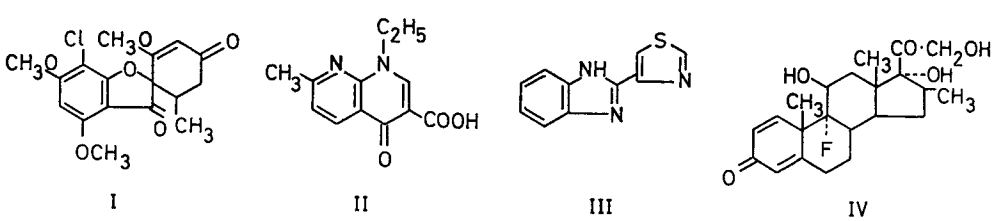


FIG. 1. Variation of mobility with pH for griseofulvin I, nalidixic Acid II, thiabendazole III, and betamethasone IV.



Nalidixic Acid shows a positive charge at low pH attributed to protonation of the =N- group, the gradual increase of negative charge to pH 7 is consistent with the ionization of the –COOH group- the plot gives a pKa value of 5·75 which agrees with the reported value of 6·0 Winningham, Nemoy & Stamey, 1968). Nalidixic Acid slowly goes into solution