

Table 1. *Peptization of liquid crystal by hydrotropes.*

Hydrotropic Salt	Concentration (mol/100g) $\times 10^3$	Hydrotropic Salt	Concentration (mol/100g) $\times 10^3$
$C_6H_{11}N^+H_3Br^-$	8.5	$Pr_4N^+Br^-$	9.4
$Me_4N^+I^-$	3.5	$Bu_4N^+Br^-$	24.2
$Me_3N^+Br^-$	4.9	$Pe_4N^+Br^-$	51.0
$Me_3N^+Cl^-$	6.2	$I^-Me_3N^+C_6H_{13}N^+Me_3I^-$	2.0
$Et_4N^+I^-$	3.5	$Br^-Me_3N^+C_6H_{13}N^+Me_3Br^-$	2.8
$Et_4N^+Br^-$	5.0	$Cl^-Me_3N^+C_6H_{13}N^+Me_3Cl^-$	3.3
$Et_4N^+Cl^-$	6.4	$Br^-Me_3N^+C_{10}H_{20}N^+Me_3Br^-$	3.1

The peptizing action of cyclohexylammonium bromide, a salt used in previous studies (Lawrence & Pearson, 1967), is exceeded by the Me_4N^+ and Et_4N^+ salts and by the highly active bis-quaternary ammonium salts; the effect decreases in the counter-ion sequence $I^- > Br^- > Cl^-$ in each case. The activity of the tetra-alkylammonium bromides shows a marked decrease after Et_4N^+ and proton magnetic resonance studies confirm the greater penetration of the higher members into the hydrocarbon regions of the smectic liquid crystals layers. Near infrared spectroscopy indicated that the wider rôle of water structure was involved in the peptization mechanism rather than a simple hydration effect. In addition to possible relevance to biological systems, the studies may provide a basis for a novel approach to the formulation of pharmaceutical preparations containing high concentrations of surfactants.

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Micellar interactions of bile salts with alkyltrimethylammonium bromides

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Numerous biologically-active quaternary ammonium compounds are surface-active. In the intestine these may interact with anionic bile salts to form ion-pairs, mixed micelles or insoluble complexes, which may influence bioavailability and reactivity of either species.

In this study the interaction of unconjugated bile salts, sodium cholate (NaC) and sodium deoxycholate (NaDC), with a model quaternary ammonium compound, tetradecyltrimethylammonium bromide (TTAB), was investigated at 25°. Solubility limits were determined by titrimetry. Homogenous solutions were investigated by surface tension, light scattering and viscosity. Results are summarized in the table.

System	cmc g ml ⁻¹ $\times 10^4$	M.M.W. $\times 10^{-3}$	$[\eta]$ dl g ⁻¹	System	cmc g ml ⁻¹ $\times 10^4$	M.M.W. $\times 10^{-3}$	$[\eta]$ dl g ⁻¹
NaC	51.7 ^a	$\sim 1^a$	0.039	NaDC	20.7 ^a	$\sim 2^a$	0.061
mole ratio NaC : TTAB				mole ratio NaDC : TTAB			
4:1	1.39	8.6	0.037	4:1	0.69	14.8	0.051
2:1	1.18	12.3	0.032	3:1	0.60	17.6	0.050
1:1	1.00	14.6	0.032	12:5	0.53	65.5	—
1:2	0.91	16.1	0.040	2:1	0.52	110.0	0.047
1:4	1.13	13.9	0.050	1:2	0.54	50.0	0.050
1:7	1.38	16.8	—	5:12	0.56	37.0	—
1:10	1.60	16.4	0.066	1:3	0.57	16.3	0.048
TTAB	11.1 ^b	27.3 ^c	0.077	1:4	0.67	17.7	0.052
				1:10	0.73	19.6	—

a Small, 1971; b Barry, Morrison & Russell, 1970; c Barry & Russell, 1972.

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, $[\eta]$, 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 $\text{CH}_3(\text{CH}_2)_n-(\text{OC}_2\text{H}_4)_x \text{SO}_4^- \text{Na}^+$ 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			area per molecule Å ²	α
	conductance	surface tension	Na ion activity		
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.