

above pH 8.0. There is a rapid change in mobility from  $+1.0 \cdot 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ v}^{-1}$  at pH 4.0 to  $-1.62 \cdot 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ v}^{-1}$  at pH 7.0. Strict control of pH when this substance is presented as a suspension is therefore desirable.

The positive charge at low pH shown by thiabendazole is probably due to protonation of the =N- groups; and the rise in negative mobility between pH 8.0 and 9.0 to ionization of the =NH group. Betamethasone, as expected from its structure shows a mobility pattern apparently depending solely on ion adsorption. The effect of SAA on a steady state mobility of all four drugs follows that found with polystyrene latex-SAA systems and may be typified with griseofulvin at pH 7.0. A single SAA e.g. sodium dodecyl sulphate, causes an increase in negative charge with concentration. Mixtures of non-ionic/ionic SAA's compete for the adsorption sites depending on the appropriate adsorption energies of the different types and their concentrations.

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## Viscometric studies on surface agent solutions and the examination of hydrophobic interactions

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Micelles as formed in aqueous solutions of surface active agents (SAA), are suitable models for studying hydrophobic interactions.

Liquid water forms spatial clusters by means of intermolecular hydrogen bonding. On addition of a SAA solute the number of bonds increases and the water molecules become more ordered around the solute molecules forming hydrogen bonded 'microscopic icebergs' around the hydrocarbon 'tail', (Nemethy, 1967), thus causing an increase in viscosity of the solution. An abrupt change in viscosity occurs at the critical micelle concentration (cmc) due to release of these ordered water molecules associated with the monomer. Measurement of viscosity is therefore a suitable method for cmc determination with obvious advantages for non-ionic SAA. SAA studied were alkyl trimethyl ammonium bromides CxTAB with x 10, 12, 14 or 16, prepared synthetically from alkyl bromides and trimethylamine and purified by recrystallization from alcohol-benzene mixtures, and commercial polyoxyethylene monohexadecyl ethers C<sub>16</sub>E<sub>y</sub>, the average value of y given as 10, 18, 30 and 60, purified by a distribution method (Weibull, 1960). Purities of all SAA's were checked using surface tension concentration plots. Viscosity measurements were carried out at 25° using an Ostwald capillary viscometer and densities determined using a pycnometer. Cmc values were obtained by plotting reciprocal reduced viscosities versus concentration. Intrinsic viscosities  $[\eta]$  at the cmc were, found from plots of reduced viscosity  $\eta_{sp}/c$  versus concentration minus the cmc (c-co). Results are shown below:—

SAA	cmc $10^{-5} \text{ mol dm}^{-3}$			SAA	cmc $\text{mol dm}^{-3}$		
	$1/\eta_{sp}/c.v.c.$	$\gamma \log C$	$[\eta] 10^2 \text{ g dl}^{-1}$		$1/\eta_{sp}/c.v.c.$	$\gamma \log C$	$[\eta] 10^2 \text{ g dl}^{-1}$
C16E10	5.60	6.00	3.9	C10TAB	$6.5 \times 10^{-2}$	$6.0 \times 10^{-2}$	6.0
C16E18	3.89	3.85	5.4	C12TAB	$1.68 \times 10^{-2}$	$1.9 \times 10^{-2}$	6.9
C16E30	2.40	2.20	7.5	C14TAB	$3.70 \times 10^{-3}$	$3.4 \times 10^{-3}$	8.2
C16E60	1.40	1.15	11.7	C16TAB	$8 \times 10^{-4}$	$8.8 \times 10^{-4}$	9.6

Cms's obtained from viscosity determinations agree with those found by surface tension measurement. The cmc values for CxTAB's compare favourably with literature values and show that the cmc decreases as the size of the hydrophobic group increases. There is a

decrease in cmc with the non ionic SAA's as ethylene oxide chain length increases, this is unexpected and is contrary to the results found by El Eini, Barry & Rhodes (1973) but agrees with results reported by Carless, Challis & Mulley (1964). The differences between the results found here and those reported in former work are presently being investigated. Possible explanations include the presence of impurities (Elworthy, Gyane & Macfarlane, 1969), surface ageing and the decreasing solubility of the ethylene oxide portion with increasing molecular weight (Schick, Atlas & Eirich, 1962). The adsorption of surfactant onto the glassware, which only occurs in small quantities, does not affect the cmc values.

Intrinsic viscosity values for the non-ionics compare favourably with the results reported by El Eini & others (1973).

Hydrophobic interactions are being investigated by the addition of small quantities of organic additives (alkyl ureas and alcohols) to the SAA solutions. The addition of aliphatic alcohols to C12TAB solutions causes a decrease in cmc, the effect increasing as alcohol chain length increases; the corresponding  $[\eta]$  values follow a similar pattern, these results can be attributed to the effect of alcohols on water structure.

However for a given concentration of alcohol  $[\eta]$  increases with increasing alcohol chain length. This can be explained by the different alcohols altering the shape of the micelle such that the axial ratio  $a/b$ , and consequently  $[\eta]$ , are affected.

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#### Correlation of phase inversion temperature with stability of oil-in-water emulsions stabilized by (polyoxyethylene)<sub>4</sub> cetyl ether

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Oil-in-water emulsions containing 30% w/w liquid paraffin, 3% w/w (polyoxyethylene)<sub>4</sub> cetyl ether (Texofor A4), and from 0.1% w/w to 10.0% w/w sodium chloride have been examined.

Phase inversion temperatures (P.I.T.) of the emulsions were determined by the programmed temperature rise viscometric technique described previously (Sunderland & Enever, 1972), and also by monitoring their conductivity-temperature relations whilst heating them under the same programmed temperature conditions.

Emulsion stability was assessed by measurement of globule coalescence rates. The number of globules per ml of emulsion was determined at various times by a photomicrographic method, and linear relations were obtained when the logarithm of globule count was plotted against time. Stability was also determined by long term storage of the emulsions.

The P.I.T. values of the emulsions ranged from 53.5° (0.1% w/w sodium chloride) to 30.5° (10.0% w/w sodium chloride), and the relation between P.I.T. and sodium chloride concentration was curvilinear. The P.I.T. values determined by the conductivity method agreed well with those obtained by the viscometric technique.

The apparent viscosity-temperature relations of the emulsions containing from 0.1 to 6.0% w/w sodium chloride also showed an additional discontinuity at approximately 35°. Microscopic examination and ultra-centrifugation studies showed that this was due to the