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CONDUCTOMETRIC STUDY OF INTERACTION BETWEEN DYES AND SURFACE ACTIVE AGENTS

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ABSTRACT

The interaction of anionic surface active agents e.g. sodium decyl sulphate (SDS), sodium dodecyl sulphate (SODS), sodium tetradecyl sulphate (STDS), sodium hexadecyl sulphate (DUDS) and sodium octadecyl sulphate (DODS) with cationic dyes, methylene blue (MB), crystal violet (CV) acridine orange (AO), rhodamine 6G (Rh 6G) and quinacrine dihydrochloride (OD) has been studied in three regions by conductometric titration. In the first region ionpair association occurs and the species (cationic and anionic) exist in equilibrium with homogeneous solution. In the second region complexation occurs by 1:1 with MB, CV and AO and by 2:1 with OD and Rh 6G forming a hetrogeneous phase, separation and equilibration containing free ions and ion-pair. In the third region the micelle formation occurs by the excess of anions in the presence of cations as well as ion-pair formation and separated complex ions that give solubilization of the complex to a homogeneous clear solution.

Introduction

In designing pharmaceutical dosage forms the interaction between large organic anions and cations is an important factor in determining the phsiochemical characteristics, compatibility, stability and availability of drug substances. The use of ionic surfactants in pharmacy for solubilization, preservation and stabilization in the presence of excipients or drugs of opposite charge may result in several desirable or undesirable interactions. The incorporation of the dyes in pharmaceutical preparations is usually considered to be the material of choice. The interaction of dyes with surface active agents depends on the distribution of chain length in the dye. The longer the chain length the greater the concentration effect. It is advantageous to use lower chain length surfactants to minimise the interaction (Mukerjee and Mysels 1955, Barry and Russels 1972).

The extensive use of dyes in pharmaceutical preparations imparts attractiveness to the product as well as antibacterial preservation (Zissman 1957).

The anionic surfactants at low concentration act as dissociated electrolytes with their free ionisable group e.g. $SO4.^{2}$. The alkyl chain behaves like the hydrocar moiety in aqeuous solution and the dimerization occurs between alkyl sulphate through hydrocarbon interaction (Mukerjee 1958, Mukerjee and Mysel 1958). The large organic dye acts as a cation. The positive charge of the dye is embedded in the anionic portion of the surfactants that results in the complexation.

In the present work interaction of some dyes with anionic surfactants of different alkyl chain length has been studied using conductometric method.

Materials and Methods

Sodium dodecyl sulphate was purchased from BDH, Poole, England. It was crystallized several times from ethanol and then purified by extraction with petroleum ether (Boiling range 40° - 60°) for 100 hours and dried in a vacuum oven at room temperature (Hikota et al., 1971). All other surfactants were purchased from Cambrian Chemicals, Croydon, England and were used as such. The cationic dyes, methylene blue, crystal violet, acridine orange, rhodamine 6G and quinacrine dehydrochloride were purchased from Sigma and were used as such. Freshly prepared doubled distilled water from an all glass still was used for the preparation of all solutions and had a specific conductivity 0.8×10^{-6} to $1.0 \times 10^{-}$ $ohms^{-1}$ cm^{-1}.

An automatic conductometric titration apparatus consisting of a Wayne Karr B 624 universal bridge connected to a conductivity cell (cell constant 1.5) was dipped in a thermostated cell. The temperature was maintained at 25°C ± 0.1 by water circulation from a thermostated bath. The conductivity was read directly from the bridge and was recorded on a chart as a continuous trace. The delivery of the titrant was maintained constant using a motorised syringe. The syringe had wide range of delivery rates according to the capacity of the syringe. The delivery of the syringe was calibrated drawing the liquid into a dried and previously calibrated 10 ml volumetric flask (A-grade).

50 cm^{-3} of the dye solution 5×10^{-4} mole dm^{-3}) were placed in the titration vessel (a jacketed thermostated beaker) maintained at 25°C ± 0.1. The conductivity cell was introduced into the solution. The addition of the standard surfactants solution (0.04 mol dm^{-3}) was made by means of a motorised automatic syringe. The chart speed was 1 cm min^{-1} and full scale deflection corresponded to 10×10^{-6} per ohm measured conductivity. The flow rate of the titrant was adjusted to a rate of 4.4×10^{-2} cm^{-2} min^{-1} at 25°C. At the end of the titration the chart was returned to the starting point and a similar curve was

traced for the titration of the standard SDDS solution in 50.0 cm^{-3} double distilled water using the same conditions.

Results and Discussion

A typical conductivity curve for the titration of SDDS against a solution of acridine orange is shown in Figure 1. It consists of three regions. At the start when SDDS concentration is low there is a linear relationship between the concentration of SDDS and specific conductivity. In this region there will be a clear solution of conductive ionic species of the dye and non-dissociated dye ion-pair which are not conductive. The other ionic species are introduced by the addition of the surfactants and the presence of undissociated surfactants (Mukerjee et al., 1958).

A second region started by a break in the curve and the solution changes to turbid at this point followed by a curvelinear region. The sudden change in the specific conductivity and volume of the titrant is due to the separation of a complex between surfactant and the dye. For a constant concentration of the dye and increasing concentration of the surface active agent the intensity of this turbidity is increased to a maximum and then is decreased rapidly until a clear solution is once more obtained. This maximum and sudden decrease in turbidity is attributed to the formation of micelles by surfactant (in the presence of dye) and the solubilization of the complex in the interior of the micelle (Mukharyar Daves 1977). This shows a 1:1 stoichrometric solubility product (K_s). The change occurring in this end point has been studied with different concentrations of the dye and is presented as double logarithem plot in Figure 2. The gradient of the straight line is 1.0 indicating that a 1:1 complex is formed with MB, CV and AO and 2:1 complex with QD and Rh 6G.

A third region occurs when the CMC of the surfactant is reached. This shows another change in the slope of the conductivity. The change is less distinct than the complexation point. At the CMC the complex solubilizes and the turbid solution be-comes clear.

All alkyl sulphate anions appear to interact with each of the dye used. An increase in the alkyl chain length of the anion results in an enhanced interaction and a decrease in the solubility of the complex as indicated by the solubility product. The change in solubility product with alkyl sulphate chain length is shown in Figure 3. The change occurs in the Ks by a constant factor of 3.6 by each methylene group added to the alkyl chain. All the surfactants appear to interact with each dye and each additional CH_2-provides a constant increment of -320 KJ mol^{-1} to the free energy of the complexocation process (Kukhayar 1983). The log K_s is linearly related to the carbon number (n) of the alkyl chain length with each dye. This shows that the conductometric end point determination is a distinct method to study the interaction between dye and surfactant of different alkyl chain length.

Table I
Relationship between K_s and the carbon atom of an alkyl chain of the anion with different cation dyes

Dye	C_n	K_s	Corelation Coefficient
Rhodamine 6G (Rh 6G)	10	2.45×10^{-8}	
	12	3.20×10^{-9}	0.999
	14	3.85×10^{-10}	
	16	4.35×10^{-11}	
Acridine Orange (AO)	10	1.10×10^{-8}	
	12	2.34×10^{-9}	0.99
	14	4.00×10^{-10}	
	16	8.56×10^{-11}	
Quinacrine Dihydrochloride (QD)	10	2.48×10^{-12}	
	12	2.00×10^{13}	0.999
	14	1.96×10^{-14}	
	16	2.05×10^{-15}	
Crystal Violet (CV)	10	1.13×10^{-8}	
	12	2.08×10^{-9}	0.998
	14	2.17×10^{-10}	
	16	3.84×10^{-11}	
Methylene Blue (MB)	10	1.04×10^{-8}	
	12	1.06×10^{-9}	0.995
	14	1.25×10^{-10}	
	16	2.81×10^{-11}	

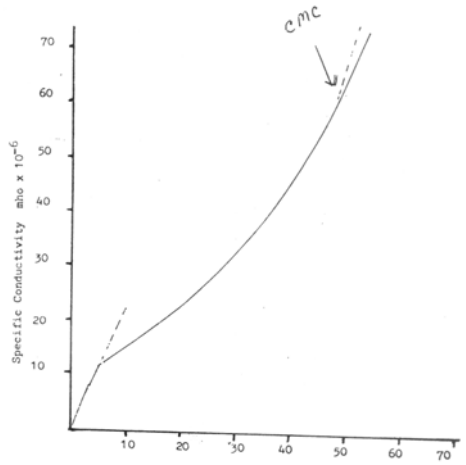

Fig. 1: Conductometric titration of sodium dodecyl sulphate (0.04 mol dm^{-3}) against Acridine orange (0.00005 mol dm^{-3}).

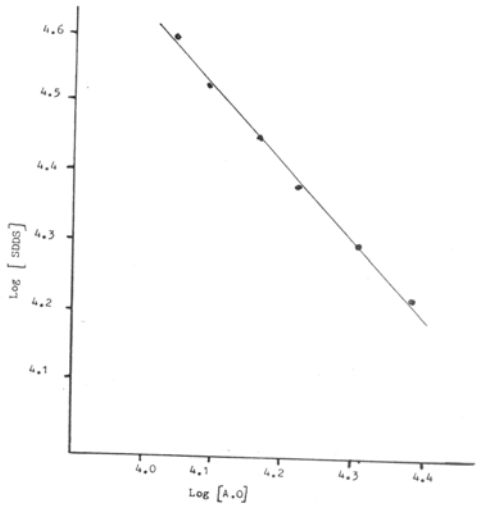

Fig. 2: Titration of sodium dodecyl sulphate against different concentration of Acridine Orange (double log plot).

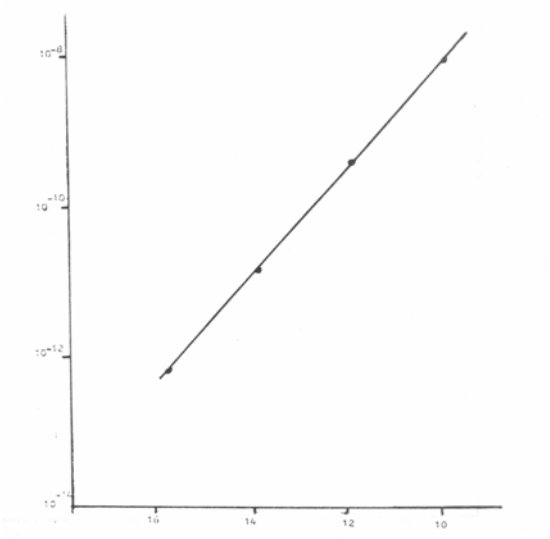

Fig. 3: K_s verses chain length for the interaction of sodium dodecyl sulphate acridine Orange.

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