Rates of Adsorption of Wetting Agents and Detergents at 'Graphon' Solution Interface

THE sodium salts of α-sulpho fatty esters (R CH(SO_3Na)-COOR') behave as either wetting agents or as detergents depending on the length of the acid and alcohol chains (R and R'). In practice, if either R or R' is long and the other chain short, then the surfactant behaves as a detergent; if both R and R' are of the same medium chain length, then the surfactant functions as a wetting agent. The ability of a compound to act as a detergent was rated on the basis of 'Terg-O-Tometer' tests and wetting ability was assessed using the Draves test[1,2].

A physical chemical approach was sought to uncover the differences between wetting agents and detergents. Thermodynamic factors, such as co-areas at the air/water and oil/water interfaces and heats of adsorption at the solid/liquid interface (refs. 3 and 4 and unpublished work by A. C. Zettlemoyer), did not differ significantly. It was recognized that a kinetic factor might distinguish between the two varieties of surfactants. A simple measurement to make was the rate of adsorption to the 'Graphon' (a graphitized carbon black with B.E.T. nitrogen surface area 104 m^2/g) surface by following the conductivity decrease with time after the graphitic powder was dispersed into the surfactant solutions (above their critical micelle concentrations, CMCs).

The α-sulpho fatty esters studied were prepared by Stirton, Weil and their co-workers (refs. 3 and 4) and were purified; they are listed in Table 1.

Table 1. THE α-SULPHO ESTER SURFACTANTS STUDIED

Compound	R	R	No. of carbon atoms $R+R'+2$
Wetting agents			
(1) Sodium hexyl α-sulphopelargonate (Na Hex αS Pelar)	7	6	15
(2) Sodium heptyl α-sulphopelargonate (Na Hep αS Pelar)	7	7	16
(3) Sodium octyl α-sulphopelargonate (Na Oct αS Pelar)	7	8	17
Detergents			
(4) Sodium methyl α-sulphomyristate (Na Me αS M)	12	1	15
(5) Sodium methyl α-sulphopalmitate (Na Me αS Palm)	14	1	17
6) Sodium ethyl α-sulphopalmitate (Na Et αS Palm)	14	2	8

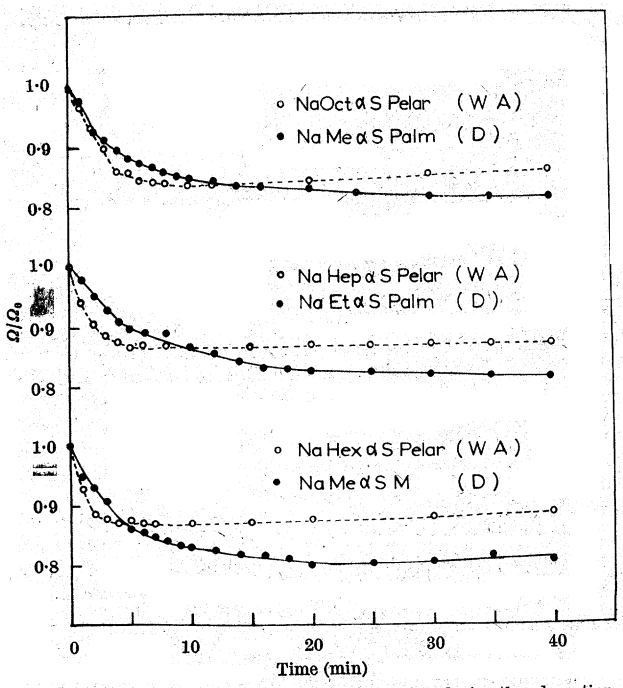

Fig. 1. Changes of reduced conductance with time during the adsorption of wetting agents and detergents at 'Graphon'/solution interface. ○, Wetting agents (WA); ●, detergents (D).

Thus compounds 1,4 and 3,5 form exact pairs as far as the number of carbon atoms are concerned. Solutions of $5{\cdot}8 \times 10^{-3}$ moles (about 0·2 per cent) (well above their CMCs) were prepared with triply distilled water and bulbs containing 1 g of activated 'Graphon' (evacuated at 105° C in 10^{-5} torr vacuum for 4 h and then sealed off) were broken in 150 cc of the surfactant solutions, with a plastic enclosed magnetic stirrer in operation. All the experiments were done at a temperature of $25° \pm 0{\cdot}1°$ C. The reduced conductances—that is, the ratio of measured (Ω) to initial conductance (Ω_0)—are plotted against time in Fig. 1. The plots indicate a clear difference between the two varieties of surfactants. The wetting agent solutions reached a minimum conductance in about 3–7 min while the detergent solutions required about 20–25 min.

It is doubted that demicellization is the slow process in the case of detergents because demicellization rates of surfactants are reported to be almost instantaneous[5]. A more probable reason for this interesting observation is that the rates of diffusion of the detergent type species

to the surface are slower than for the wetting type. For the detergent solutions, a slow ageing and thus a slow decrease in surface tension with time was also noted at the air/water interface (ref. 3 and unpublished work); no such ageing effect was noted for the wetting agent type.

It is known that the adsorption of surfactant anions takes place with the hydrocarbon portion of the anion oriented toward the hydrophobic surface of 'Graphon' and the polar group projected into the bulk liquid phase. Another possible reason for the slow rates of adsorption of the detergent type species is because the chains R and R' are of different length; re-arrangement of the ions for the proper orientation at the interface may be delayed. In other words, the sticking coefficient of the detergent type species could be lower than those of the wetting agent type.

Diffusion measurements with radioactively labelled species would allow these two factors, diffusion rates and the sticking factor to be separated.

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