LETTER TO THE EDITOR

Cleavable Surfactants Derived from Poly(ethylene glycol) Monomethyl Ether

Sir:

In your Journal, Yue *et al.* (1) have published a paper on cleavable surfactants derived from poly(ethylene glycol) monomethyl ethers. The authors have informed the reader on only two papers devoted to noncyclic acetal-type surfactants. Although contributions on this type of surface-active agents are indeed few, they go beyond the two articles mentioned by the authors. Kuwamura and Takahashi (2) were the first to report on surface-active acetals with the general formula $RCH[O(C_2H_4O)_mH]_2$ ($R=C_8H_{19} \div C_{16}H_{33}$; $m = 2–6$). In a subsequent paper, these authors described similar compounds with two oligooxyethylene chains terminated with methoxyl groups (3). The described acetals showed surface properties, i.e., they are soluble in water, form micellar solutions, and exhibit typical characteristic properties of nonionics. Other homologous, noncyclic acetals with the general formula $RCH[O(C_2H_4O)_wR^1]_2$ ($R=H$, $CH_3 \div n\text{-}C_9H_{19}$; $w = 1–4$; $R^1 = CH_3 \div n\text{-}C_5H_{11}$) were reported later (4–8).

We pay special attention to the results of the hydrolysis kinetics reported by Yue *et al.* (1). The authors have stated that they have determined "the kinetic constants of the micelles." In fact, the reported pseudo first-order rate constants *k* represent an average of the rate constants for micellar and unaggregated surfactants. Besides the reported data are expected to be smaller than those for unaggregated systems. Such an assumption seems to be supported by the data obtained from kinetic studies of the hydrolysis of homogeneous acetals with the structure $RCH[O(C_2H_4O)_wR^1]_2$ (6), which does not form micellar solutions (4,7). For example, the *k* value for $C_5H_{11}CH[O(C_2H_4O)_3CH_3]_2$ estimated at pH = 3 (HCl solution) and 25°C is $2.0 \cdot 10^{-4}\ s^{-1}$ [$6.24 \cdot 10^{-4}\ s^{-1}$ at pH = 2 and 20°C (6)], whereas the recalculated values for surfactants **Ia** and **Ib** (1) are $3.3 \cdot 10^{-6}\ s^{-1}$ and $28 \cdot 10^{-6}\ s^{-1}$, respectively. Furthermore, the results reported (6) show that the increase of the alkyl chainlength R (from CH_3 to $n\text{-}C_5H_{11}$) causes small increases in hydrolytic reactivity, whereas the change of the oligooxyethylene chainlength within the range from 1 to 4 oxyethylene units does not affect the susceptibility to hydrolysis of the acetals studied. Finally, Kuwamura and Takahashi (2) investigated the hydrolysis kinetics of $C_{11}H_{23}CH[O(C_2H_4O)_5H]_2$ in HCl solutions by the cloud-point depression method. They pointed out, too, that the pseudo first-order rate constant *k,* equal to $5.5 \cdot 10^{-6}\ s^{-1}$ in micellar solution (after recalculating from 1 $mol^{-1}\ s^{-1}$ units), is markedly smaller in comparison with rate constants reported in the literature for hydrolysis of nonmicellizing acetals (9). Similar observations have been made by Jaeger *et al.* (10), who investigated hydrolysis of cyclic acetal-type cationic surfactants.

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