COMMUNICATIONS

Evidence for the intrusion of polyoxyethylene into the hydrocarbon core of non-ionic surfactant micelles

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The intrinsic viscosities, [η], of non-ionic surfactants of structure, $CH_3[CH_2]_{m-1}[OCH_2OCH_2]_{1.25m}OH$, were measured in water at 298 K. [η] increased linearly with hydrocarbon chain length from m = 3 to m = 15, and between m = 17 and m = 31. There was a discontinuity between m = 15 and m = 17, which was attributed to intrusion of some polyoxyethylene into part of the hydrocarbon core for surfactants in which m > 15. This effect gave a micellar hydration which was lower than expected for the higher members of the series. Other factors relevant to the intrusion of polyoxyethylene into hydrocarbon are discussed.

Studies on the solubilization of azobenzene, menaphthone, cortisone acetate and griseofulvin in polyoxyethylene alkyl ethers of the type $CH_3[CH_2]_{m-1}[OCH_2CH_2]_{1.25m}OH$, showed that maximum uptake was in the $C_{16}E_{20}$ compound. Solubilization in C_8E_{10} was roughly half, and in $C_{32}E_{41}$, approximately one third of the maximum value (Elworthy & Patel 1982). On ascending the series, the first compound showing a decreased solubilization over its predecessor was $C_{18}E_{22}$, which is the first compound whose hydrocarbon chain is not liquid at 298 K. As the hydrocarbon chain needs to be liquid for micellization and normal solubilization to occur (Arnarson & Elworthy 1980), it was suggested that some of the polyoxyethylene intruded into the core to maintain liquidity (Elworthy & Patel 1982). This would have the effect of moving the core/polyoxyethylene–water boundary further out in the micelle, thus diluting this region in terms of its polyoxyethylene content, and so reducing solubilization, which mainly occurs in this region. The intruded micelle would have a lower hydration than a non-intruded one, as a shorter length of the polyoxyethylene chain is now available for hydration.

Materials and methods

The preparation of the surfactants C_8E_{10}, $C_{12}E_{15}$ and $C_{14}E_{18}$ was reported by Elworthy & Patel (1982). The methods of measuring viscosity and partial molar volume were those of Patel (1982).

Results and discussion

Fig. 1 gives the plots used in determining the intrinsic viscosity, [η], for the above three surfactants. Values of [η] for C_4E_6 and C_6E_6 are from Elworthy & Florence (1965), for $C_{16}E_{18}$ from Patel (1982), for $C_{16}E_{21}$ from Macfarlane (1970), for $C_{16}E_{22}$ from Elworthy (1960), for $C_{18}E_{22}$ from Elworthy & Patel (1982), for $C_{22}E_{27.5}$ interpolated from Arnarson & Elworthy (1980), and for $C_{32}E_{41}$ from Arnarson & Elworthy (1981) and are plotted in Fig. 2.

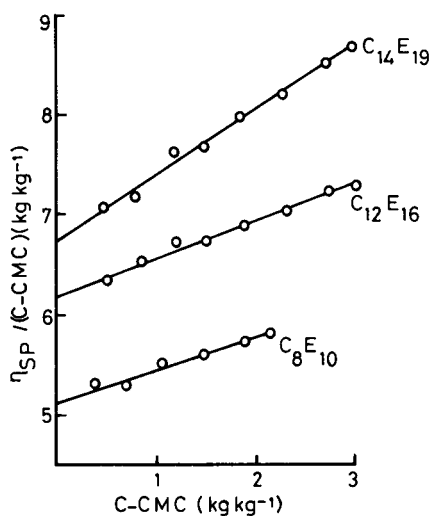FIG. 1. Reduced viscosity against micellar concentration for C_8E_{10}, $C_{12}E_{16}$ and $C_{14}E_{19}$.
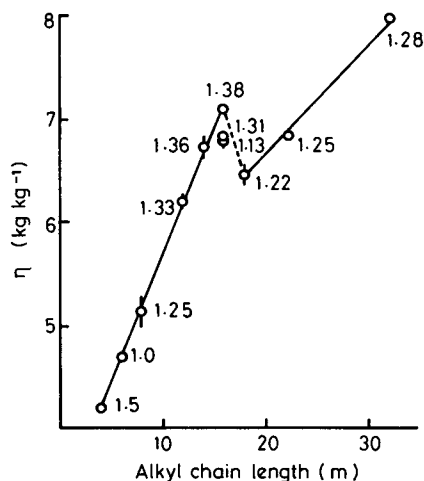
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FIG. 2. Intrinsic viscosities, [η], of $C_mE_{1.25m}$ surfactants at 298 K, with the actual E/C ratios placed by the points. The error bars represent 95% confidence limits. For sources of data see text.

The points fall into two sets with a discontinuity between C_{16} and C_{18}. On the assumption that the micelles were spherical, which seems likely for reasons previously stated (Elworthy & Patel 1982), the micellar hydrations (w) were calculated from the standard equation (Tanford 1961). A graph of w against alkyl chain length has exactly the same shape as Fig. 2; w increases linearly with m up to C_{16}, having a value of 6.0 mol H_2O mol^{-1} oxyethylene for $C_{16}E_{22}$, decreasing to a value of 5.2 mol H_2O mol^{-1} oxyethylene for $C_{18}E_{22}$, then starts to increase again. This behaviour would be consistent with intrusion beginning at C_{18}, giving a micellar core consisting of hydrocarbon plus some anhydrous polyoxyethylene, which leaves less polyoxyethylene to be hydrated in the mantle of the micelle than is normally the case. Intrusion moves the core/mantle boundary outwards in the micelle, which reduces the polyoxyethylene content of the mantle, and renders it a poorer region for solubilization, compared with a non-intruded micelle having a more concentrated polyoxyethylene-water region.

As the melting points of the hydrocarbon part of the surfactants rise with increasing chain length, the extent of intrusion may also increase in order to maintain the liquid core necessary for micellization. It may be that C_{22} and C_{32} surfactants owe their water solubility to this effect: with ionic surfactants C_{16} is the largest hydro-phobe in surfactants soluble at 298 K. As the hydrocarbon chain is lengthened in non-ionic surfactants, increased intrusion thus causes poorer and poorer environments to develop for the solubilization of drugs in the polyoxyethylene-water region, and explains the decreased solubilization found above C_{16} (Elworthy & Patel 1982).

Two other factors are relevant to the idea of intrusion. First, solubility experiments show that n-octane and dimethoxytetraoxyethylene glycol are miscible in all proportions, indicating that the type of mixing required by the intrusion effect in the micelle can occur. Second, while the heats of dilution of polyoxyethylene glycols in water are exothermic, the main enthalpic contribution is from the hydroxy groups (Kagemoto et al 1967). When these groups are blocked, as they are in the relevant part of the surfactant structure, entropic effects, arising from the loss of water structure from around the polyoxyethylene chain as it is drawn into the hydrocarbon core, might be expected to predominate. Bayley & Koleske (1976) report that polyoxyethylene will partition from water into chloroform due to the disordering of the polymer chain and loss of the water structure.

While the intrusion effect clearly merits further study, it does explain the anomalous viscosity and solubilization results observed as the hydrocarbon chain is lengthened above 16 carbon atoms.

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