# Studies of Solubilized Micellar Solutions

## III. The Viscosity of Solutions Formed with Nonionic Surfactants

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Viscosity studies have been carried out on a series of oil/water solubilized micellar solutions (so-called "microemulsions") of liquid paraffin, glycerol, water and blends of Tween 60 and Span 80. The variation of relative viscosity, $\eta_{rel}$, with volume fraction, $\phi$, of the micelles conformed to

$$\eta_{rel} = \exp[a\phi/(1 - k\phi)],$$

where $a$ is a constant and $k$ is the hydrodynamic interaction coefficient. The value of $k$ was found to be independent of micellar diameter over the range 13.3 to 48.6 nm. Decrease in the surfactant/glycerol molar ratio of the solution from 0.231 to 0.028 produced a linear decrease in $k$ from 1.10 to 0.62. For $\phi \leqslant 0.15$, an exponential relationship existed between $\eta_{rel}$ and the surfactant concentration. The effect of the surfactant concentration on the viscosity has been discussed in terms of the interaction between the polyoxyethylene chains at the surface of the micelles. Allowance for the hydration of the polyoxyethylene chain, reduced the value of $a$ towards the theoretical value of 2.5 for solid spheres. Increase of the Tween/Span molar ratio from 1.0 to 1.6 had no significant effect on the values of $a$ or $k$.

### INTRODUCTION

Many equations have been proposed to describe the concentration dependence of viscosity in dispersed systems (1) and several workers have reported their application to the class of solubilized micellar solutions often referred to as "microemulsions." In a study of water/oil micellar solutions of potassium oleate, water, benzene and hexanol, Bowcott (2) has shown that the viscosity data could be fitted to an equation proposed by Roscoe (3) for a system of uniformly sized spheres.

$$\eta_{rel} = (1 - 1.35\phi)^{-2.5}, \qquad [1]$$

where $\eta_{rel}$ is the relative viscosity and $\phi$ is the volume fraction of the micelles. Matsumoto and Sherman (4) have reported the application of Eq. [2] to oil/water micellar solutions of benzene, water, Tween 20 and Span 20.

$$\eta_{rel} = \exp a\phi/(1 - k\phi) \qquad [2]$$

$a$ is a constant with a theoretical value of 2.5 for solid spheres and $k$ is a hydrodynamic interaction coefficient. Equation [2] was derived by Mooney (5) and extensively tested by Sweeney and Geckler (6). This equation was shown to adequately describe the viscosity data for the micellar solutions after modification to allow for the amount of benzene solubilized within the micelles of excess emulsifier. $k$ was shown to depend empirically on the modal diameter, $d_m$, of the micelles according to

$$k = 1.079 + \exp(0.01008/d_m) + \exp(0.00290/d_m^2). \qquad [3]$$

Other workers have reported factors which influenced the parameter, $k$. Mooney assumed $k$ to be dependent on the relative radii of the dispersed particles and theoretically predicted a range $1.35 < k < 1.91$ for spheres. Saunders (7) used an equation of the same form as Eq.

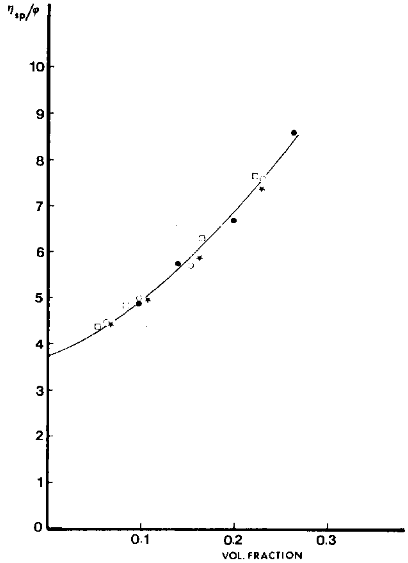


FIG. 1. Reduced viscosity vs micellar volume fraction for solutions with a molar surfactant/glycerol ratio of 0.050 and liquid paraffin concentrations of (—○—) 0.124; (—★—) 0.220; (—●—) 0.297; (—□—) 0.360 g oil/g oil + surfactant + glycerol.

[2] in a study of the viscosity of a series of monodisperse polystyrene latices and showed a decrease in $k$ from 1.357 to 1.118 with increasing particle diameter from 0.099 to 0.871 $\mu$m. He concluded that $k$ was determined by other factors than simple geometric packing and, in particular, since the particles were charged, it was suggested that the observed effect was due to the electroviscous effect which would increase with decreasing particle size.

In a previous investigation (8), the micellar size of solubilized micellar solutions of liquid paraffin, glycerol, water, Tween 60 and Span 80 was reported as a function of the liquid paraffin concentration, the surfactant/glycerol ratio and the Tween /Span ratio. The visocity of these systems has now been determined and the factors affecting the hydrodynamic interaction coefficient have been discussed.

## EXPERIMENTAL METHODS

### *Preparation of Solutions*

The solubilized micellar solutions were identical to those previously studied by light scattering (8) and consisted of oil/water systems of liquid paraffin, Tween 60, Span 80, glycerol and water. The solutions were prepared by stirring together weighed quantities of all the constituents at 70°C for 5 min. The systems were then allowed to cool to room temperature with constant stirring. Solutions with molar surfactant/glycerol ratios of 0.231, 0.169, 0.091, 0.050 and 0.028 were prepared in which the surfactant consisted of an equimolar mixture of Tween 60 and Span 80. For each surfactant/glycerol ratio, four solutions with differing oil content were prepared and each of these was diluted with water to give a further five systems with concentrations varying over a range suitable for viscosity studies. Similar systems were prepared with Tween/Span molar

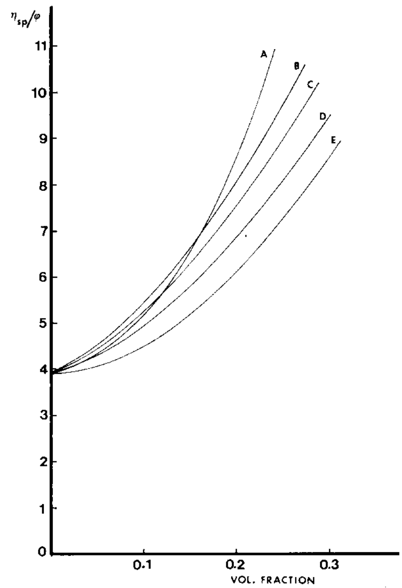


FIG. 2. Representative curves of reduced viscosity vs volume fraction for solutions with molar surfactant/glycerol ratios of (A) 0.230; (B) 0.169; (C) 0.091; (D) 0.050 and (E) 0.028.