Studies of Solubilized Micellar Solutions

I. Phase Studies and Particle Size Analysis of Solutions Formed with Nonionic Surfactants

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The preparation and physical properties of oil/water solubilized micellar solutions (so-called "microemulsions") containing liquid paraffin, glycerol, water and blends of Tween 60 and Span 80 have been examined. Turbidity-spectra methods of particle sizing have shown that an increase of temperature of preparation over the range 25–80°C led to a gradual decrease in the modal diameter and the half-width of the size distribution curve. Phase diagram studies on micellar solutions prepared at 70°C have indicated a pronounced dependence of the area of existence of clear solutions on the ratio of Tween to Span in the system and on the oil content. Light-scattering investigations on these systems have indicated micelle diameters of between 13 and 45 nm. In general, micellar size was increased by increasing the oil content and by decreasing the surfactant/glycerol ratio. No significant effect on micellar diameter was detected as the Tween/Span molar ratio was varied between 1.0 and 1.6.

INTRODUCTION

The oil/water and water/oil solubilized micellar solutions termed "microemulsions" by Hoar and Schulman (1) are readily distinguished from emulsions by their transparency and more fundamentally by the fact that they represent single thermodynamically stable solution phases in contrast to the thermodynamically unstable two-phase systems constituting emulsions. The micellar size of these systems has been estimated by various methods including electron microscopy (2), X-ray diffraction (3), turbidity-spectra methods (4) and light scattering (5, 6). In this investigation we have used light scattering to determine the micellar size of oil/water solutions similar to those previously studied by Osipow (7), consisting of liquid paraffin, glycerol and water, together with blends of the nonionic surfactants Tween 60 and Span 80. In particular, the effect on micellar size caused by variation of the oil concentration, the surfactant/glycerol ratio and the Tween/Span ratio have been

investigated and correlated with the effect of these variables on the isotropic solution region of the phase diagrams. Early work on these systems showed that there was an optimum temperature of preparation giving maximum clarity of a solution containing a given nonionic surfactant. This fact has recently been reiterated by Shinoda and Kunieda (8) who showed a similar increase of clarity with decrease in the oxyethylene chain length of the nonionic surfactant at a fixed temperature. The effect of the temperature of preparation on the particle size distribution of the systems studied in this investigation is reported.

EXPERIMENTAL METHODS

Materials

Commerical (Honeywill-Atlas Ltd., Carshalton, Surrey, England) samples of Tween 60 [polyoxyethylene (20) sorbitan monostearate] and Span 80 (sorbitan monooleate) were used as received. For the purposes of calculation, effective molecular weights of 1310 and 430,

respectively, were assumed for these inhomogeneous detergents. The liquid paraffin was a purified grade complying with the specifications of the British Pharmacoepia. Glycerol (May and Baker Ltd) had a refractive index and density at 20°C of 1.4750(1.4746) and 1.257(1.2613) g ml^{-1}, respectively.

Phase Diagram Studies

The areas of existence of clear micellar solutions of liquid paraffin, glycerol, water and Tween 60/Span 80 blends were determined. Weighed quantities of all constituents were mixed at 70°C for 5 min and then allowed to cool, with constant stirring, to room temperature. Each solution was prepared individually and the criterion for solution formation was taken to be the production of an optically clear, fluid system. Solutions were prepared with a range of oil concentrations and a fixed Tween/Span molar ratio of 1.0 and also with Tween/Span molar ratios of 1.3 and 1.6 and a fixed oil concentration of 16% (w/w).

Turbidity Measurements

Turbidity measurements were made with a Unicam SP 500 spectrophotometer modified by collimation of the light beam to reduce errors arising from the acceptance of scattered light (9). The walls of the 4 cm turbidity cells were blackened to minimize errors due to reflection of scattered light. The effect of temperature of preparation on the particle size was ascertained using a solution with 16% (w/w) liquid paraffin and an equimolar mixture of Tween 60 and Span 80, constituting approximately 23% (w/w) of the total solution. The surfactant, oil and water were stirred at 70°C for 5 min to form a crude emulsion. The preparation of a clear solution from this emulsion was then attempted at a range of tempratures between 25 and 80°C. The emulsion was brought to the required temperature and glycerol (11%, w/w), prewarmed to this temperature, was added. The system was then allowed to cool, with stirring, to room temperature.

The turbidity, t, of a series of volume fractions, ϕ, of each system was measured over a wavelength range of $\lambda = 550$ to 700 nm. The particle size distribution was calculated using the turbidity-spectra method (10, 11) which assumes a size distribution curve described by the function

$$Cf(r) = (r - r_0) \exp\left[-(r - r_0)/s\right]^3, \quad [1]$$

where $Cf(r)dr$ is the number of particles per unit volume with a radius between r and $(r + dr)$, C is a normalization constant and r_0 is the radius of the smallest particles present in consequential numbers. s determines the modal radius r_m and the half-width w, through the relations $w = 0.9015s$ and $s = \sqrt{3}(r_m - r_0)$. The experimental turbidity data at each wavelength were extrapolated to infinite dilution and plots of $(\lambda t/\phi)_\lambda/(\lambda t/\phi)_{\lambda_R}$ against λ were constructed where λ_R denotes a reference wavelength of 546 nm. These experimental spectra were compared with spectra derived using the expression

$$(\lambda t/\phi)_0$$

$$= \frac{3\pi \int_p^\alpha \Sigma(\alpha)(\alpha-p) \exp\left\{-\left[(\alpha-p)/q\right]^3\right\} d\alpha}{\int_p^\alpha \alpha^3(\alpha-p) \exp\left\{-\left[(\alpha-p)/q\right]^3\right\} d\alpha},$$

where α, p, and q are given by $\alpha = 2\pi r/\lambda$, $p = 2\pi r_0/\lambda$ and $q = 2\pi s/\lambda$. Values of $(\lambda t/\phi)$ for the required p and q values were interpolated from tables of computed values for the correct relative refractive index and normalized by dividing by corresponding values at the reference wavelength. The p and q values were varied systematically until the best fit between the theoretical and experimental spectra was obtained.

Light-Scattering Measurements

A series of solutions with surfactant/glycerol molar ratios of 0.231, 0.169, 0.091, 0.050 and 0.028 was prepared, all of which had a Tween/Span molar ratio of 1.0. These systems are represented by the lines A to E, respectively, in Fig. 1. For each surfactant/glycerol ratio a
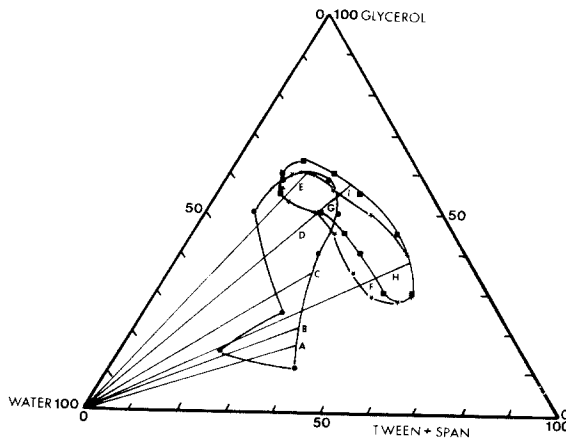
FIG. 1. Partial phase diagram of water–glycerol–Tween 60/Span 80 (total 100%) with 10% (w/w) liquid paraffin showing areas of existence of clear homogeneous oil/water micellar solutions prepared with Tween/Span molar ratios of (——●——), 1.0; (——★——), 1.3; and (—-■—-), 1.6. Diagram shows composition of systems selected for light-scattering measurements (see text).

range of four solutions, each with different oil content, were prepared. Each of these four systems was diluted with water to give a further five solutions with concentrations varying over a range suitable for light-scattering measurements. Similar systems, represented by F and G (Fig. 1) with a Tween/Span ratio of 1.3 and H and I with a Tween/Span ratio of 1.6 were prepared such that systems represented by lines D, G and I had an identical surfactant/glycerol ratio. The surfactant/glycerol ratio of systems F and H was 0.132.

Solutions were clarified by filtration through 0.1 μm Millipore filters and the light scattered by the solutions at room temperature was measured using a Fica 42000 photogonio-diffusiometer (A.R.L.Ltd.) at a wavelength of 546 nm. The scattering, S_{90}, in excess of that of the solvent was measured at a scattering angle of 90° and corrected for depolarization of the incident light by the Cabannes factor.

RESULTS

Figure 1 shows the changes in the area of existence on the phase diagram of solutions containing 10% (w/w) liquid paraffin, caused by varying the Tween/Span molar ratio between 1.0 and 1.6. Clear solutions with Tween/Span ratios of less than 1.0 could not be prepared.

Figure 2 shows the change in the area of existence of systems with an equimolar Tween/Span mixture, when the oil content was varied from 10 to 25% (w/w). The boundary of the 25% (w/w) system was ill-defined at high surfactant concentrations because of gel formation. The approximate boundary between fluid and gel systems is denoted by a broken line.

Theoretical and experimental graphs of $(\lambda l/\phi)_\lambda / (\lambda l/\phi)_{\lambda_R}$ against λ for each temperature of preparation are shown in Fig. 3. A minimum radius, r_0, of 10 nm was assumed for all calculations. It was not found possible to fit the experimental lines for systems prepared at 25 and 30°C. The theoretical broken line shown in Fig. 3 for these systems represents the maximum value of r_m (350 nm) for which $(\lambda l/\phi)$ values could be interpolated from the tables and the micelles have radii which are clearly in excess of this limiting value. At the highest temperatures (60, 70 and 80°C), the experimental lines could all be represented by theoretical lines for radii of between 20 and 35 nm. These latter values are higher than
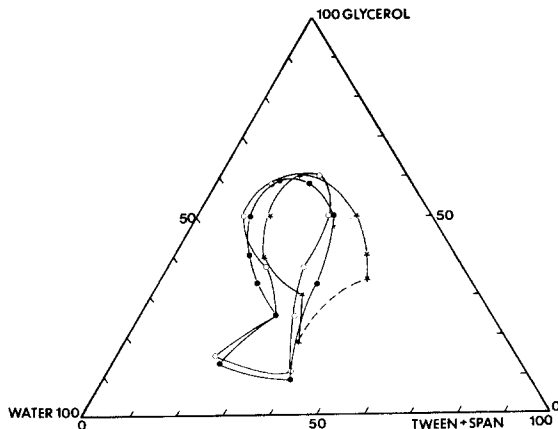
FIG. 2. Partial phase diagram of water–glycerol–equimolar Tween 60/Span 80 mixture (total 100%) showing areas of existence of homogeneous solutions prepared with liquid paraffin concentrations of (--○--) 10% (w/w); (--●--) 15% (w/w); (--★--) 25% (w/w).

those indicated by light-scattering measurements on systems of similar composition prepared at 70°C. The r_m values calculated from
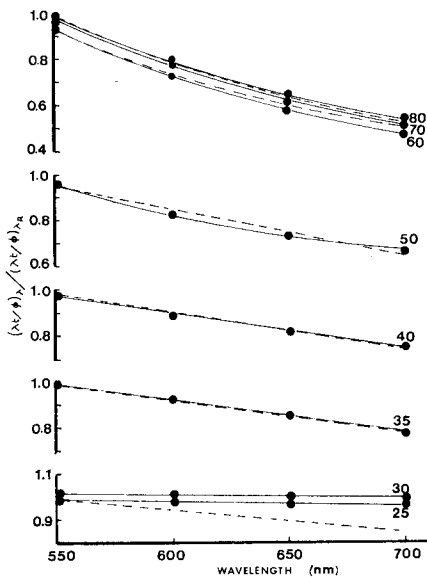

FIG. 3. Comparison of theoretical (– –) and experimental (——) turbidity-spectra graphs for micellar solutions prepared at different temperatures.

the turbidity data for systems of low micellar size were, however, found to be dependent on the value assigned to r_0, and consequently are approximate values only. Values of r_m and w (calculated using Eq. [1]) are given in Table I. Increase in the temperature of preparation caused a decrease in both of these parameters. This is attributable to an increase in solubilizing power of the nonionic detergents as their cloud point is approached (8). At the higher preparation temperatures there is also an increased possibility of hydrolysis or trans-esterification reactions which may contribute to the observed decrease in micellar size.

The micellar size in the system with varying surfactant/glycerol molar ratios was deter-

TABLE I

EFFECT OF TEMPERATURE OF PREPARATION ON THE PARTICLE SIZE DISTRIBUTION

Preparation temp (°C)	Modal radius r_m (nm)	Half-width w (nm)
35	200	297
40	150	175
50	45	55
60 ⎫		
70 ⎬	23	20
80 ⎭		

(5 4)

mined from the limiting values of c/S_{90} in the normal manner. The concentration, c, refers to the total weight of micellar components per milliliter of solution. In the calculation of c, the glycerol was regarded as a component of the micelle although, more correctly, its distribution between the micelles and aqueous solvent should be considered. Figure 4 shows the increase of particle diameter, calculated assuming micellar sphericity, caused by an increase of the oil concentration at each surfactant/glycerol ratio. At a given oil concentration, increase of the surfactant/glycerol ratio initially caused a decrease in micellar diameter. For all systems, the diameter became essentially independent of this ratio above a certain limiting value. Figure 4 also incorporates results for systems with Tween/Span molar ratios of 1.3 and 1.6 and indicates that over this limited range, the Tween/Span ratio had no significant effect on micellar size.

DISCUSSION

The pronounced effect on the area of existence on the phase diagram caused by the increase of the Tween/Span ratio from 1.0 to 1.6 may be related to the relative concentrations of Span and glycerol in the systems. Figure 1 shows that at glycerol concentrations <55–60% (w/w) increase in the Tween/Span ratio of the system was accompanied by an increase in the Tween/glycerol ratio required for solution formation. This may be demonstrated numerically by considering the range of Tween/glycerol ratios over which systems containing, for example, 30% glycerol, formed solutions. The maximum and minimum Tween/glycerol ratios were 0.80 and 0.65 for the equimolar Tween/Span system; 1.43 and 1.30 for the 1.3:1 Tween/Span system and 1.54 and 1.33 for the 1 6:1 Tween/Span system. Osipow (7) noted a similar effect for oil/water solutions of Tween 60, Span 80, mineral oil, 2-ethylhexanediol-1,3 and water and related it to the opposing effects which Span and alcohol had at the oil/water interface. Addition of Span
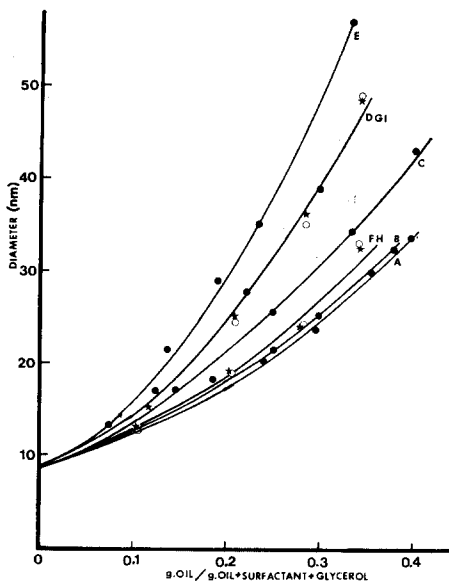

FIG. 4. The effect of liquid paraffin concentration on the micellar diameter of solutions with surfactant/glycerol molar ratios of (A) 0.231; (B) 0.109; (C) 0.091; (D) (G) (I) 0.050; (E) 0.028; (F) (H) 0.132 and with Tween/Span molar ratios of —●—, 1.0; —★—, 1.3 and ⸱⸱⸱○—, 1.6.

caused condensation of the interfacial film while alcohol caused the film to expand.

The effect of the relative concentrations of glycerol and surfactant on the micellar diameter is shown in Fig. 4. The decrease in diameter following an increase in the surfactant/glycerol ratio at a fixed oil content is due to the solubilization of the oil within a larger number of Tween/Span micelles, which are consequently swollen to a lesser extent. The attainment of a limiting micellar diameter at high surfactant/glycerol ratios and the failure of solutions to form when this ratio was further increased (Fig. 1) demonstrate the necessity for a minimum quantity of glycerol in the solution.

Increase in the liquid paraffin concentration is seen to cause a movement of the area of existence towards regions of higher surfactant

concentration (Fig. 2) and also an increase of micellar diameter (Fig. 4). The latter effect is a consequence of the swelling of the micelle core following the incorporation of the increased quantities of oil. Incorporation of solubilizate within the hydrocarbon core of a surfactant micelle has been shown, in many cases, to lead to an increase in the number of surfactant molecules in the micelle (12). It was suggested that the excess surfactant molecules were required to cover the expanded hydrophobic micellar core. The same reason will be applicable to the solutions under discussion and explains why solutions with the higher liquid paraffin concentrations will form only at regions of higher surfactant concentration.

ACKNOWLEDGMENT

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Studies of Solubilized Micellar Solutions

II. Phase Diagram Studies and Particle Size Analysis of Solutions Formed with an Ionic Surfactant

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Phase diagram studies have been carried out on oil/water solubilized micellar solutions (so-called "microemulsions") containing sodium oleate, amyl alcohol, water and varying amounts of liquid paraffin. The isotropic solution regions have been defined. Light-scattering measurements have indicated an increase in micellar diameter following an increase in the concentration of liquid paraffin and a decrease in the surfactant/alcohol ratio. Estimations of the composition of the micelles have revealed that, although this increased diameter resulted mainly from an increase in the liquid paraffin content of the micelle, there were also increases in the concentrations of the other micellar components which contributed to the size increase. The molecular ratio of alcohol to sodium oleate at the micellar surface varied between 2.3 and 3.0. No significant dependence of this ratio on the liquid paraffin concentration or the bulk surfactant/alcohol ratio was noted.

INTRODUCTION

Light-scattering methods have been used by several workers for the determination of micellar size in the type of solubilized micellar solutions often referred to as "microemulsions." In their estimation of the particle size of water/oil micellar solutions of potassium oleate, p-methyl cyclohexanol, benzene and water, Schulman and Friend (1) noted a decrease in light scattering as the concentration of micelles was increased, indicative of considerable interference of the light scattered by neighboring particles. They proposed an empirical treatment of the data based on Eq. [1],

$$\log d = \log d_0 - Bc, \qquad [1]$$

where B is a constant, c is the concentration, d is the apparent diameter and d_0 is the true diameter of the particles. In a previous paper (2), we have applied conventional light-scattering equations in the determination of the particle size in oil/water solubilized micellar solutions containing nonionic surfactants. We now report the determination of micellar size in oil/water solubilized micellar solutions containing sodium oleate, liquid paraffin, amyl alcohol and water with compositions varying over the clear fluid solution region, as determined by phase diagram studies.

The necessity of producing an interfacial film on the emulsion droplets of a suitable constitution to allow the development of a metastable negative interfacial tension was stressed in the early work on these systems (3). Bowcott and Schulman (4) determined those ratios of alcohol to surfactant at the oil/water interface which were necessary for micellar solution formation. A series of water/oil systems stabilized with straight-chain and cyclic alcohols were analyzed and interfacial, molecular alcohol/surfactant ratios ranging from 1:1 to 3:1 were reported. The value of the ratio was found to depend on the amount of water dispersed by the system and also on the chain length of the alcohol. Shah (5) has proposed that at a 3:1 molecular ratio a 2-dimensional

hexagonal arrangement of molecules exists at the interface which favors micellar solution formation. Estimations of this interfacial packing ratio have been carried out in the systems studied here, based on an assumed distribution of components between the lipophilic (micelle core), amphiphilic (interfacial region) and hydrophilic (aqueous) regions of the solution.

EXPERIMENTAL METHODS

Materials

Sodium oleate (B.D.H. Chemicals Ltd.) was purified by recrystallization from ethanol/water mixtures and dried to constant weight, mp 226°C (232–235°C). Amyl alcohol was reagent grade (May and Baker Ltd) with a density and refractive index at 20°C of 0.810(0.824) g ml⁻¹ and 1.4100(1.4100), respectively. The liquid paraffin was a purified grade conforming to the specifications of the British Pharmacoepia.

Phase Diagram Studies

Phase diagram studies on the liquid paraffin, sodium oleate, amyl alcohol, water system have been carried out to determine the oil/water micellar solution region. Solutions were prepared at room temperature by dissolving the sodium oleate in water, adding the liquid paraffin and titrating this crude dispersion to clarity with amyl alcohol. The criterion for successful solution formation was taken to be the production of an optically clear, fluid system which appeared nonbirefringent when viewed through crossed polaroids. At high alcohol concentrations, inversion to water/oil systems, involving in some cases an intermediate liquid crystalline state, was noted. The upper limits of the isotropic oil/water regions were determined from graphs of conductivity vs composition, an inflection point occurring when systems inverted from a highly conducting, water-continuous solution to a less-conducting, oil-continuous solution. The effect on the area of existence of varying the liquid paraffin concentration of the solution from 5 to 20% (w/w) was determined.

Light-Scattering Measurements

A series of solutions with sodium oleate/alcohol molar ratios of 0.105, 0.129 and 0.150 were selected for measurement. The systems are represented by the lines A, B and C, respectively, on the phase diagram (Fig. 1). It was not possible to examine systems with
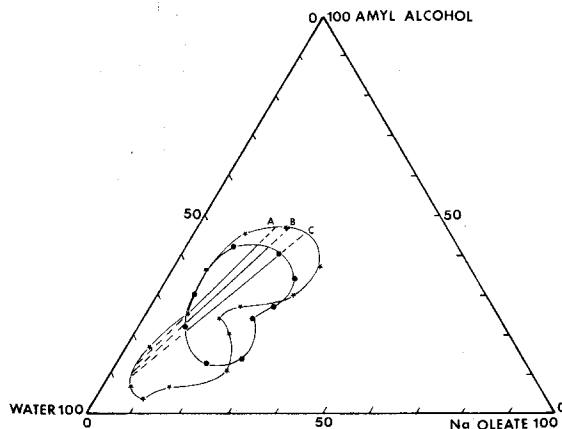

FIG. 1. Partial phase diagram of water–amyl alcohol–sodium oleate (total 100%) showing areas of existence of oil/water solubilized micellar solutions prepared with liquid paraffin concentrations of (— ★ —) 5% (w/w) and (— ● —) 20% (w/w). Diagram shows composition of systems selected for light-scattering measurements (see text).

higher surfactant content, and thereby cover the whole solution region, since such systems were too viscous to enable meaningful measurements to be carried out. For each of the three surfactant/alcohol ratios, four subseries were prepared in which the oil content of the solution was varied between 10 and 40% (w/w). Each of these subseries was further subdivided into five solutions in which the sodium oleate/alcohol/liquid paraffin ratio was maintained at the required value, but in which the total concentration of these components was varied over an appropriate range. Because of practical difficulties· experienced in the dilution of these micellar solutions with water, each of these solutions was prepared directly, although they do in fact represent "dilutions" of the original solutions. Wherever possible, solutions were filtered through 0.22 μm Millipore filters, but for the more concentrated systems, filters of larger pore size were required because of the high viscosity. The light scattered by the solutions at room temperature was measured using a Fica 42000 photogoniodiffusiometer (A.R.L.Ltd.) at a wavelength of 546 nm. The scattering, S_{90}, in excess of that of the solvent, was measured at a scattering angle of 90° and corrected for depolarization of the incident light by the Cabannes factor.

RESULTS

Figure 1 shows the regions of existence of oil/water solubilized micellar solutions containing 5 and 20% liquid paraffin, and indicates a pronounced movement towards regions of higher surfactant and alcohol with increase of oil content.

The concentration dependence of the scattering ratio, S_{90}, for solutions with a surfactant/alcohol molar ratio of 0.150 and varying oil concentrations is shown in Fig. 2. The solution concentration is expressed as the total weight of micellar components per milliliter of solution. All lines terminate at the lowest concentration at which microemulsions would form. Similar graphs were obtained for the two other surfactant/alcohol ratios. These graphs are typical of those reported by Schulman and Friend (1), the apparent decrease in S_{90} at high concentration being the result of destructive interference of the scattered light. The empirical equation proposed by these authors was used in the treatment of the light-scattering data. Apparent diameters were calculated
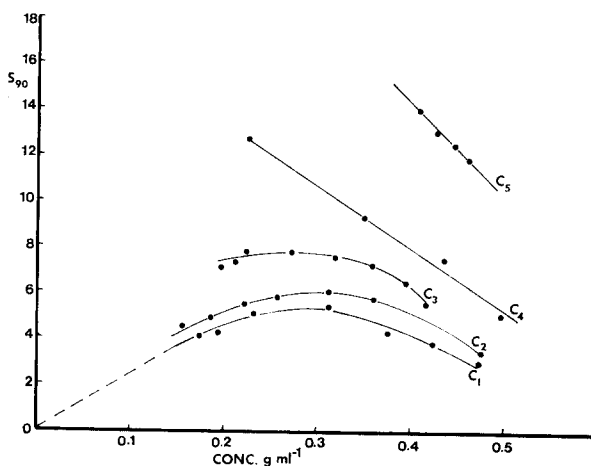

Fig. 2. Concentration dependence of the scattering ratio for solutions with a sodium oleate/alcohol molar ratio of 0.150 and with liquid paraffin concentrations of C_1, 0.140; C_2, 0.186; C_3, 0.225; C_4, 0.290; C_5, 0.356 g oil/g oil + surfactant + alcohol.
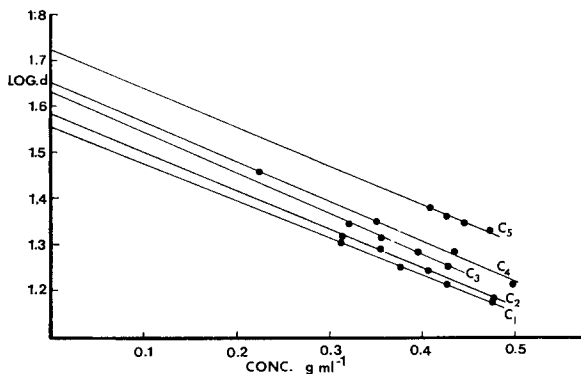
FIG. 3. Log apparent micellar diameter vs solution concentration for micellar solutions with a sodium oleate/alcohol molar ratio of 0.150 and with liquid paraffin concentrations of C_1, 0.140; C_2, 0.186; C_3, 0.225; C_4, 0.290; C_5, 0.356 g oil/g oil + surfactant + alcohol.

from c/S_{90} ratios using conventional light-scattering equations and assuming micellar sphericity. Plots of log d against c were linear (see Fig. 3) and d_0 values were obtained by extrapolation to zero concentration according to Eq. [1]. Where data were available at sufficiently low concentrations to allow extrap-
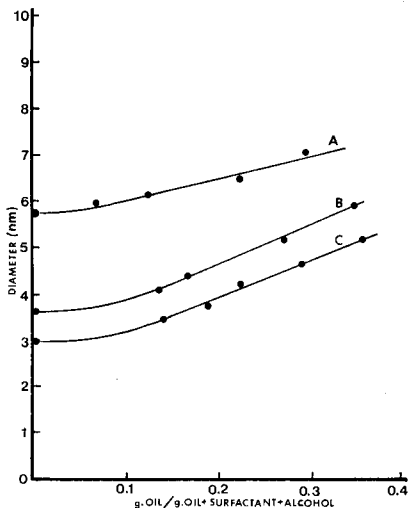

FIG. 4. Effect of liquid paraffin concentration on the micellar diameter of solutions with sodium oleate/alcohol molar ratios of (A) 0.105; (B) 0.129 and (C) 0.150.

olation of graphs of c/S_{90} vs c to zero concentration, d_0 values were calculated in the normal manner. Agreement between d_0 values calculated in this manner and those obtained by application of Eq. [1] was reasonable. For example, a d_0 value of 3.4 nm was calculated using Eq. [1] for system C_1, which compares with a corresponding value of 2.6 nm calculated from the limiting value of c/S_{90}.

Figure 4 shows the increase in micellar diameter which resulted from an increase in the oil content and a decrease in the surfactant/alcohol ratio. The increase in diameter at zero oil content was due to the incorporation of increasing amounts of alcohol into the mixed surfactant/alcohol micelle as the alcohol content of the system was increased.

DISCUSSION

By making assumptions concerning the distribution of the components between the intermicellar liquid (hydrophilic region), the micellar surface (amphiphilic region) and the micellar core (lipophilic region), it was possible to determine the way in which the composition of the micelle varied with increasing oil content. The critical micelle concentration of sodium oleate is very low [0.07 g dl^{-1} (6)] relative to the concentrations present in the micellar solutions. Since the pure soap also

has a very low solubility in liquid paraffin, it was assumed to be located entirely at the micellar surface. Similarly, the solubility of amyl alcohol in water is again rather low (3.18 g dl^{-1} at 20°C) and for convenience it was assumed that the alcohol distributed itself exclusively between the micellar core and the micellar surface or amphiphilic layer. It was further assumed that the amount of oil incorporated in the micellar surface could be neglected. This is probably the least valid of the assumptions since one of the requirements for "microemulsification," as postulated by Schulman, Stoeckenius and Prince (3) is that some oil should be able to associate with the interfacial film. Using this simplified model of the micellar solution, the composition of the amphiphilic layer was estimated in the following manner. The total interfacial area is governed by the amount of sodium oleate in the system, since all of this compound is required to be accommodated at an interface, and also by the amount of alcohol which is associated with the surfactant at the interface. For any assumed molecular ratio of alcohol/sodium oleate in the interface, the surface area per alcohol/sodium oleate complex was calculated using surface areas of 0.30 and 0.20 nm^2, reported for sodium oleate and straight-chain alcohol molecules, respectively, at an oil/water interface (4). The micellar core is composed of the oil, which was assumed to be uniformly distributed throughout all micelles, and the remainder of the alcohol not associated with the interface. By adjusting the ratios of alcohol/sodium oleate in the interface it was possible to arrive at a description of the system in which all the surfactant could be accommodated at the surface of micelles, the composition of which was such as to give a micellar weight in agreement with that indicated by light-scattering measurements. The molecular ratios of alcohol/sodium oleate for varying oil content and varying surfactant/alcohol bulk ratios, calculated by this method, are given in Table I. The values all fall within the range (1:1 to 3:1) previously determined (4) for water/oil micellar solutions prepared with potassium

TABLE I

Ratio of Amyl Alcohol and Sodium Oleate at Micellar Surface

Molar sodium oleate/alcohol ratio in system	Oil content g oil/g oil +surfactant +alcohol	Molar alcohol/ sodium oleate ratio at micellar surface
0.105	0.067	2.3
	0.125	2.4
	0.221	2.5
	0.292	2.5
0.130	0.132	2.8
	0.165	2.8
	0.266	2.7
	0.345	2.7
0.150	0.140	3.0
	0.186	2.9
	0.225	2.8
	0.290	2.7
	0.356	2.8

oleate and a series of straight-chain alcohols. For any particular bulk surfactant/alcohol ratio there was an almost constant interfacial ratio, in spite of large variations in the amount of oil incorporated into the droplet. There was also very little variation in this ratio with differing bulk molar ratios of surfactant/ alcohol, indicating that the distribution of alcohol between the interface and the micellar core was determined solely by the requirements of the interface.

The change in the composition of the micelles with increase in oil content calculated for a molar surfactant/alcohol ratio of 0.150 is shown in Fig. 5. Similar graphs were obtained at the other surfactant/alcohol ratios. Figure 5 shows that although the main cause of increase in size was the incorporation of oil into the micellar core, there were also increases in the amounts of the other components, which also contributed towards the observed increase in size. The increase in concentration of the interfacial components is presumably a consequence of the expansion of the core by the oil and the necessity to provide an amphiphilic bridging region between the lipophilic (hydro-
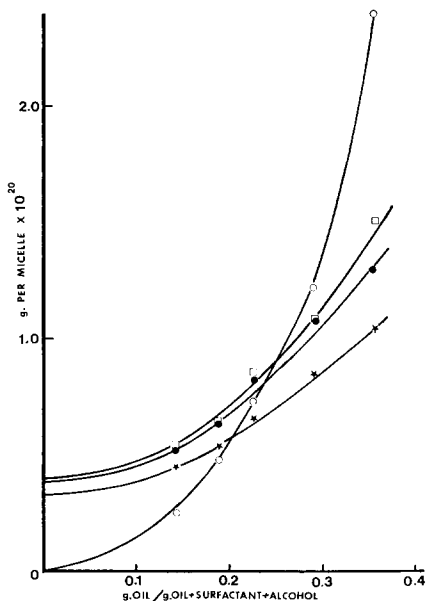
FIG. 5. Variation of the concentration of micellar components with the liquid paraffin concentration of the micellar solution. (—○—) liquid paraffin; (—★—) alcohol at micellar surface; (—●—) sodium oleate; (—□—) alcohol in micellar core.

carbon) and hydrophilic (aqueous) regions. A similar effect was observed following the solubilization of additional components into the core of micelles of a nonionic surfactant (7).

An increase in the amounts of surfactant and alcohol required for the formation of a micellar solution following an increase in the oil content of the system, is also indicated in Fig. 1. The solution region was moved away from the water

corner of the phase diagram as the oil content was increased.

The decrease in micellar size as the solution region of the phase diagram was traversed from lines A to C (i.e., as the surfactant/alcohol ratio was increased) is similar to the situation observed with solubilized micellar solutions formed by nonionic surfactants (2). As the amount of surfactant in the system is increased, a greater interfacial area is possible and the oil is thus distributed among a greater number of micelles, which are consequently smaller in size. This reasoning is no longer applicable to high surfactant/alcohol ratios, and clear micellar solutions fail to form presumably because there is an insufficient quantity of alcohol in the system to enable an interfacial film of the required composition to be formed.

ACKNOWLEDGMENT

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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, η_{rel}, with volume fraction, ϕ, 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 η_{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 η_{rel} is the relative viscosity and ϕ 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.

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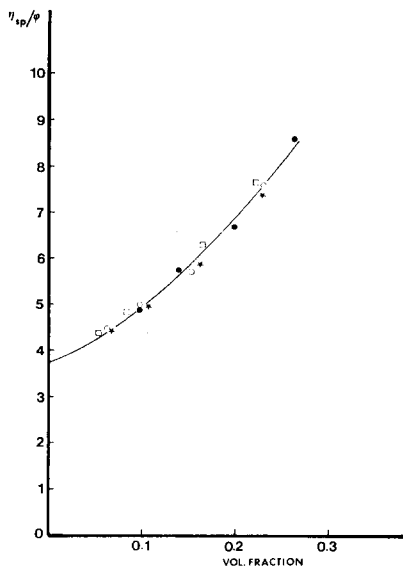
FIG. 1. Reduced viscosity vs micellar volume fraction for solutions with a molar surfactant/glycerol ratio of 0.050 and liquid paraffin concentrations of (—○—) 0.124; (—★—) 0.220; (—●—) 0.297; (—□—) 0.360 g oil/g oil + surfactant + glycerol.

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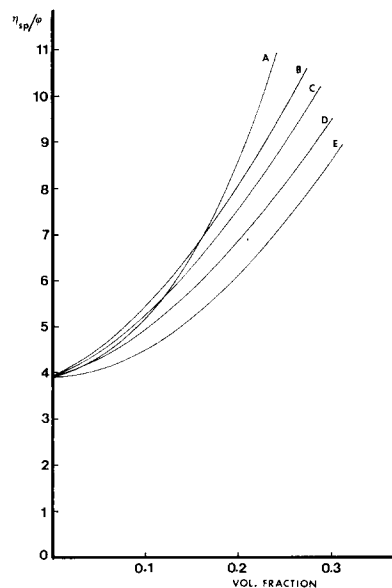
FIG. 2. Representative curves of reduced viscosity vs volume fraction for solutions with molar surfactant/glycerol ratios of (A) 0.230; (B) 0.169; (C) 0.091; (D) 0.050 and (E) 0.028.

ratios of 1.3 and 1.6 and with a surfactant/glycerol ratio of 0.050.

Viscosity Measurements

Measurements were made at 25°C using an Epprecht-Rheomat 15 rotational viscometer. All solutions were examined for non-Newtonian behavior by measuring over a range of shear rates. With the exception of the most concentrated solutions, the systems were Newtonian in behavior and the mean viscosity over the shear range was calculated. The data for the non-Newtonian systems were extrapolated to zero shear rate. The viscosity of each solution relative to water at 25°C, η_{rel}, was calculated from these mean and extrapolated values.
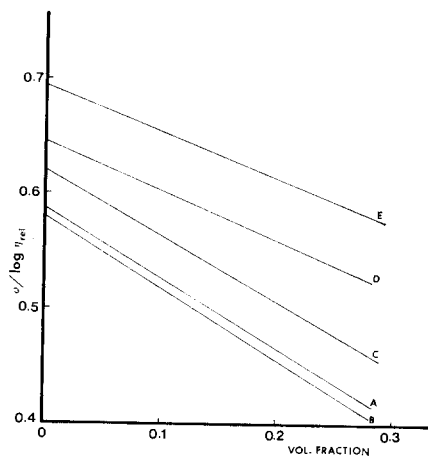

FIG. 3. Regression lines for variation of $\phi/\log \eta_{rel}$ with ϕ for solutions with molar surfactant/glycerol ratios of (A) 0.230; (B) 0.169; (C) 0.091 ;(D) 0.050 and (E) 0.028.

TABLE I

Viscosity Data for Solubilized Micellar Solutions Containing an Equimolar Mixture of Tween and Span

Molar surfactant/ glycerol ratio	Oil content g oil/g oil +surfactant +glycerol	a	k	Micellar diameter (nm)
0.231	0.238	—	—	20.5
	0.294	3.92	1.16	23.6
	0.385	3.93	1.04	32.8
	0.455	3.81	1.09	44.6
0.169	0.182	4.17	1.06	18.3
	0.297	3.98	0.99	21.1
	0.384	3.87	1.06	24.9
	0.249	3.94	0.88	32.7
0.091	0.143	4.03	0.72	17.3
	0.250	3.86	0.74	25.5
	0.333	3.73	0.85	34.4
	0.400	3.86	0.64	43.3
0.050	0.124	3.82	0.70	17.3
	0.220	3.84	0.57	27.8
	0.297	3.66	0.71	38.9
	0.360	3.72	0.74	48.6
0.028	0.071	3.58	0.63	13.3
	0.133	3.51	0.62	21.6
	0.188	3.41	0.66	28.9
	0.235	3.56	0.55	35.0

RESULTS

The viscosity results are presented as graphs of η_{sp}/ϕ (reduced viscosity) against ϕ, where η_{sp} is the specific viscosity and ϕ is the micellar volume fraction. Figure 1 shows the graph for solutions with a molar Tween/Span ratio of 1.0, a molar surfactant/glycerol ratio of 0.050 and varying oil concentrations. No significant difference between the results for solutions with differing oil content was apparent and a single curve has been used to represent all points. Similar graphs were obtained for the other surfactant/glycerol ratios. Figure 2 shows the representative curves for each of these systems and indicates that the surfactant/glycerol ratio of the solution had a significant effect on the concentration dependence of the reduced viscosity. The data were fitted to Eq. [2], rewritten in the form

$$\phi \log \eta_{rel} = 2.303/a - 2.303k\phi/a. \quad [4]$$

All systems conformed to this equation, giving linear plots of $\phi/\log \eta_{rel}$ vs ϕ, from which values of a and k were derived by linear regression analysis. Figure 3 shows the regression lines for systems with varying surfactant/

TABLE II

Viscosity Data for Solubilized Micellar Solutions with a Surfactant Glycerol Ratio of 0.050 and Tween/Span Ratios of 1.3 and 1.6

Molar Tween/ Span ratio	Oil content g oil/g oil +surfactant +glycerol	a	k	Micellar diameter (nm)
1.3	0.114	3.50	0.82	15.1
	0.204	3.43	0.76	25.3
	0.278	3.47	0.55	36.3
	0.339	3.51	0.61	47.4
1.6	0.114	3.76	0.56	14.6
	0.204	3.45	0.72	24.6
	0.278	3.33	0.81	35.1
	0.339	3.19	0.84	47.9

glycerol ratios. Values of a and k are given in Table I, together with micellar diameters previously obtained by light scattering studies on these systems. A lack of dependence of k on the diameter is apparent from these results.

The data obtained for systems with Tween/ Span ratios of 1.3 and 1.6 were treated in a similar manner and values of a and k are given in Table II. Comparison with corresponding values for the solutions with equimolar Tween/ Span mixtures shows a lack of any significant dependence of a and k on the Tween/Span ratio.

DISCUSSION

The apparent lack of correlation between k and the particle diameter, as shown by Table I, is in contrast to the observations of Matsumoto and Sherman (4). The k values determined for the systems examined here are considerably smaller than the values which might be expected if the apparent increase of k with decreasing particle diameter observed by these workers, was continued to the lower size range of the micelles studied here. Clearly, several factors may influence the value of k. Thus, if, as suggested by Mooney (5), k is dependent on the relative radii of the spheres, then the particle size distribution might be expected to affect k. In the micellar solutions of Matsumoto

and Sherman the increase in particle diameter was also accompanied by an increase in the width of the size distribution curve. It is suggested that this increase in polydispersity, rather than the increase in mean diameter, may have been the main cause of the observed decrease in k. However, because of the large number of variables in these systems and the inhomogeneity of the detergents, it is not possible to reach any definite conclusions.

A major influence on the value of k is seen to be the concentration of surfactant. The decrease in k with decrease in the surfactant/ glycerol ratio (Table I) can be shown to be linear. Sherman (9) has discussed the influence of emulsifier concentration on the relative viscosity of emulsions. In a reexamination of van der Waarden's (10) data for the viscosity of oil/water emulsions stabilized by sodium naphthasulfonates he has shown that the effect of emulsifier concentration, C, at a fixed volume fraction could be expressed by an equation of the form

$$\ln \eta_{rel} = mC + b \qquad [5]$$

where m and b are constants. Figure 4 shows that a linear relationship exists between $\ln \eta_{rel}$ and C for the system studied here, at volume fractions not exceeding 0.15. At higher ϕ values, a distinct curvature was noted. It is suggested that the major cause of the variation of η_{rel} with surfactant concentration in these systems is the interaction between the polyoxyethylene chains of the Tween molecules.

TABLE III

Mean Values of a and k for Solutions Containing an Equimolar Tween/Span Mixture, Calculated Assuming a Hydration of the Polyoxyethylene Chains of 3.6 Molecules of Water/Ethylene Oxide Group

Molar surfactant/ glycerol ratio	a	k
0.231	2.87	0.95
0.169	3.02	0.67
0.091	3.33	0.51
0.050	3.03	0.49
0.028	2.57	0.43

The decrease in the interparticulate distance with increase of ϕ increases the possibility of interaction between the polyoxyethylene chains of neighboring micelles and these interactions may contribute to the observed viscosity increases.

A considerable quantity of solvent may be mechanically trapped between the poly-

eythylene chains (11), in addition to the maximum of 2 molecules of hydrogen-bonded water (12)/ethylene oxide group. Allowing for a hydration of 3.6 molecules of water/ethylene oxide group, reduced the value of a towards the theoretical value of 2.5 for solid spheres (see Table III).
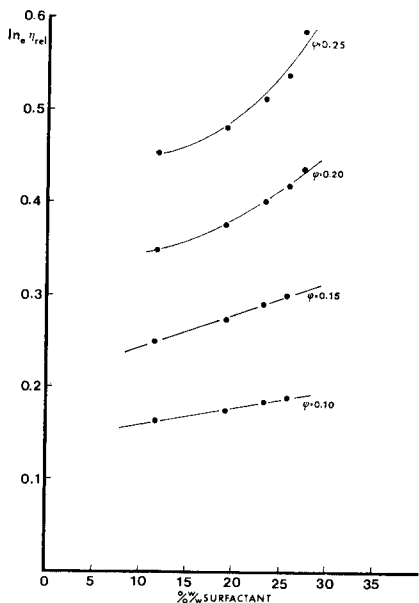
Fig. 4. Exponential relationship of relative viscosity and surfactant concentration for different volume fractions of micelles.

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