

IJP 02064

A viscosity study on oil-in-water microemulsions

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(Received 17 November 1989)

(Accepted 9 December 1989)

Key words: Microemulsion; Viscosity

Summary

The viscosity of oil-in-water microemulsions formed from isopropyl myristate, polysorbate 80, sorbitol and water has been studied as a function of oil-volume fraction, φ , surfactant and cosurfactant concentration, and surfactant:cosurfactant mass ratio. Phase studies have indicated an optimum polysorbate:sorbitol mass ratio for microemulsion formation of 1:2.5. The variation in relative viscosity, η_{rel} , with φ behaved in conformity with the equation $\eta_{rel} = \exp[a\varphi/(1 - K\varphi)]$, where a is a constant and K is the hydrodynamic interaction coefficient. It was found that a decrease in polysorbate:sorbitol mass ratio of the microemulsion produced a systematic increase in a and a decrease in K . In addition, a values increased linearly from 3.03 to 4.54 while K values decreased from 1.72 to 1.39 with increase in the polysorbate and sorbitol concentrations in the microemulsion from 30 to 45%. The increase in the constant a was attributed to the greater hydrodynamic volume of the droplets and the bound solvent layer was calculated to increase from 7 to 22% of the droplet core radius.

Introduction

Various investigations have been carried out to study the formation and stability of microemulsions (Baker et al., 1984a; Candau et al., 1986; Kahlweit et al., 1987) and various techniques have been employed to study the size, shape and interactions of microemulsion droplets (Cebula et al., 1982; Mukherjee et al., 1983; Cheung, 1987; Hou et al., 1988; Robbins et al., 1988; Chokshi et al., 1989). Viscosity studies have been applied to investigate the hydration and the importance of interactions of microemulsion droplets (Attwood et al., 1974; Siano, 1983; Baker et al., 1984b; Peyrelasse et al., 1988).

Many equations have been proposed to describe the influence on the viscosity of the volume fraction of the dispersed phase, φ , (Sherman, 1983). Several viscosity equations have been proposed on the basis that the volume fraction of the continuous phase is $(1 - K\varphi)$ such as

$$\eta_{rel} = \exp a\varphi/(1 - K\varphi) \quad (1)$$

where a is a constant with a theoretical value of 2.5 for solid spheres and K is the hydrodynamic interaction coefficient. K depends on the hydrodynamic interaction between drops and increases as the drop size decreases (Saunders, 1961). Matsumoto and Sherman (1969), using an equation of the same form, described the viscosity data for oil-in-water microemulsions of benzene, water, Tween 20 and Span 20. They obtained values of a below that of rigid spheres (1.66–2.08) and K dependent on the mean particle size. Attwood et

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al. (1974), using Eqn 1, obtained values of a between 3.19 and 4.17 and of K from 0.55 to 1.16 for oil-in-water microemulsions of liquid paraffin, glycerol, water and blends of Tween 60 and Span 80. They concluded that allowance for the hydration of the polyoxyethylene chain reduced the value of a towards the theoretical value of 2.5 for solid spheres. Baker et al. (1984b) also used Eqn 1 in the case of water-in-oil microemulsions of water, xylene, sodium alkylbenzenesulfonate and hexanol, obtaining a values of 3.3–6.0.

They reported the values of a to show an increase with higher surfactant concentration, indicating that the hydrodynamic volume of the droplets grew larger. This was ascribed to the increase in the ratio of surfactant layer thickness to droplet core radius as the surfactant concentration was increased.

In this paper, oil-in-water microemulsions formed from isopropyl myristate, polysorbate 80, sorbitol and water have been investigated. Microemulsion areas have been established as showing the influence of the polysorbate:sorbitol mass ratio on the extent of the microemulsion domain. Viscosity measurements have been carried out for a variety of microemulsions in the main region of microemulsion domains in order to determine the effect of the polysorbate and sorbitol concentrations and polysorbate:sorbitol mass ratio on the hydration of microdroplets.

Materials and Methods

Materials

D-Sorbitol (research grade) was supplied by Serva Feinbiochemica and used as received. Polysorbate 80 (polyoxyethylene 20 sorbitan monooleate, Tween 80) and isopropyl myristate (98% pure) were supplied by Sigma and used as received. In every case, water was distilled from an all-glass apparatus.

Methods

Determination of microemulsion areas. The boundaries of the microemulsion domains in isothermal triangular diagrams were determined by progressive titration of the four component mix-

tures for a series of values for the polysorbate:sorbitol mass ratio. At each value of the ratio, a mixture of polysorbate, sorbitol and isopropyl myristate, characterized by a selected value of the isopropyl myristate to polysorbate and sorbitol mass ratio, R_m , was progressively enriched in water during agitation by means of a magnetic stirrer. The concentrations of water, where turbidity-to-transparency and transparency-to-turbidity transitions occurred, were derived from weight measurements. By repeating this experiment for other values of R_m , the boundaries of the microemulsion domain corresponding to the chosen value of the polysorbate:sorbitol mass ratio were determined. All titration experiments were performed in water-jacketed beakers maintained at $55 \pm 1^\circ\text{C}$. Microemulsions of compositions within the range for transparent microemulsions remained stable for at least 2 months storage at 37°C .

Preparation of samples for viscosity measurements. Microemulsions contained 30, 35, 40 and 45% w/w of polysorbate 80 and sorbitol and a range of isopropyl myristate concentrations in the main microemulsion region. The mass ratio of polysorbate 80 to sorbitol was kept constant at 1:2.5 for microemulsions containing 30, 35 and 45% of polysorbate and sorbitol. For those containing 40% of polysorbate and sorbitol, the mass ratio of polysorbate:sorbitol was equal to 1:1.5, 1:2.0, 1:2.5 and 1:3.0. Stock solutions of sorbitol in water were titrated in the mixtures of isopropyl myristate and polysorbate 80 to yield the appropriate quantities of sorbitol, simultaneously being agitated by means of a magnetic stirrer in a water-jacketed beaker at $55 \pm 1^\circ\text{C}$. Small quantities of water were titrated in the mixtures to obtain the appropriate compositions.

Microemulsion series containing a range of isopropyl myristate concentrations were prepared using the following dilution technique in order to maintain the same polysorbate and sorbitol concentration. Parts of the microemulsion containing the highest isopropyl myristate concentration were diluted with water containing the same concentration of polysorbate 80 and sorbitol as that in the original microemulsion. The microemulsions were equilibrated at 37°C for 24 h and filtered through

0.45 μm Millipore filters before viscosity measurements.

Viscosity measurements. Measurements were carried out using Ubbelohde suspended level viscometers. The viscometer with a solvent flow time of approx. 200 s was placed in a water bath at a constant temperature of $37 \pm 0.1^\circ\text{C}$. For each microemulsion series containing a range of isopropyl myristate concentrations the flow times of the microemulsion were plotted vs. isopropyl myristate concentration and extrapolated to zero concentration. The flow time corresponding to zero isopropyl myristate concentration was used to calculate the relative viscosity (η_{rel}) of the microemulsion. The specific viscosity ($\eta_{\text{sp}} = \eta_{\text{rel}} - 1$) and the reduced viscosity ($\eta_{\text{red}} = \eta_{\text{sp}}/\varphi$) were also evaluated. φ represents the volume fraction of isopropyl myristate calculated from the weight % of this component and the densities of isopropyl myristate and microemulsion as determined by pycnometry.

Results and Discussion

Microemulsion areas

Fig. 1 shows the regions where stable oil-in-water microemulsions existed for mass ratios of polysorbate 80 to sorbitol between 1:1.5 and 1:4.0. Stable microemulsions with mass ratios of polysorbate:sorbitol outside this range could not be prepared under the experimental conditions of this study. The maximum proportion of incorporated isopropyl myristate as a microemulsion decreased on changing the value of the polysorbate:sorbitol mass ratio from 1:2.5. Also, the minimum amount of isopropyl myristate required to prepare stable microemulsions became lower for polysorbate:sorbitol mass ratios approaching 1:2.5. The largest microemulsion region was produced at a polysorbate:sorbitol mass ratio of 1:2.5. The boundaries of the microemulsions examined were almost identical to those reported for isopropyl myristate, polysorbate 60, sorbitol, water microemulsions by Attwood and Ktistis (1988). They found that a polysorbate:sorbitol mass ratio of 1:2.0 resulted in the largest microemulsion region. This difference in optimum mass ratio may

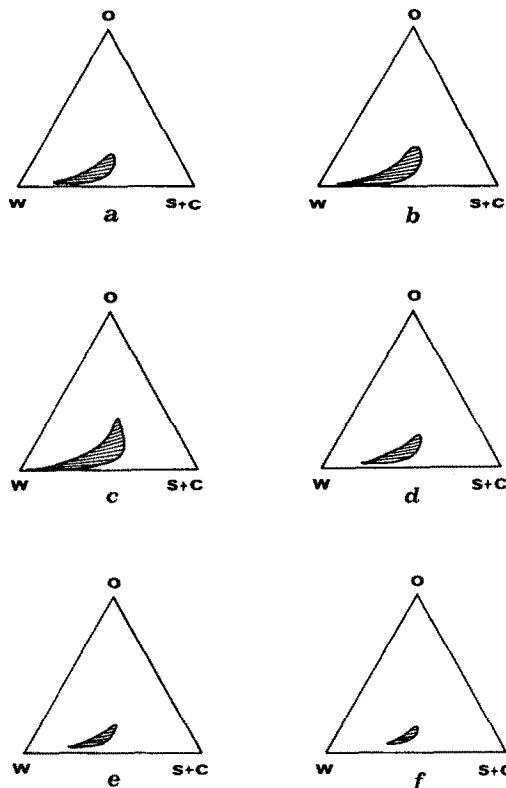


Fig. 1. Ternary phase diagrams showing areas of existence of oil-in-water microemulsions with isopropyl myristate (O), polysorbate 80 (S), sorbitol (C) and water (W) at 37°C for polysorbate:sorbitol mass ratios of: (a) 1:1.5, (b) 1:2.0, (c) 1:2.5, (d) 1:3.0, (e) 1:3.5 and (f) 1:4.0.

be attributed to the greater area per molecule of polysorbate 80 (polyoxyethylene monooleate) than that of polysorbate 60 (polyoxyethylene monostearate) and to the closer molecular packing of polysorbate and sorbitol around the oil droplet.

Viscosity results

Fig. 2 shows plots of the reduced viscosity, η_{red} , vs volume fraction of isopropyl myristate, φ , for microemulsions for various values of the polysorbate and sorbitol concentrations at the polysorbate:sorbitol mass ratio of 1:2.5. For all concentrations studied, η_{red} rises sharply with increase in φ . In addition, η_{red} increases with increasing polysorbate and sorbitol concentration at any given φ . Extrapolation of η_{red} to $\varphi = 0$ shows the effect of the polysorbate and sorbitol con-

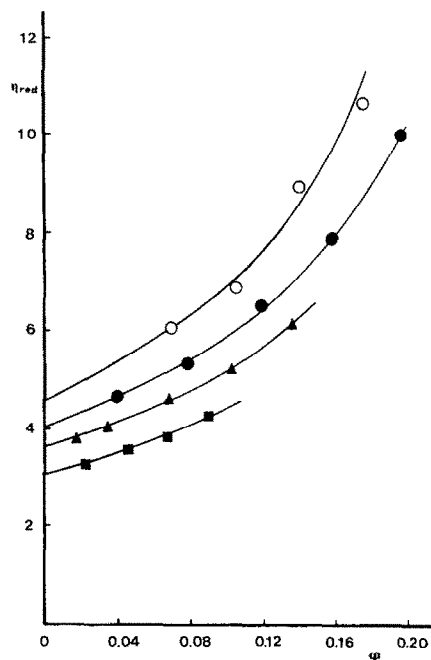


Fig. 2. Reduced viscosity, η_{red} , plotted vs isopropyl myristate volume fraction, ϕ , for microemulsions with a polysorbate:sorbitol mass ratio of 1:2.5 and polysorbate and sorbitol concentrations of (■) 30%, (▲) 35%, (●) 40% and (○) 45% w/w.

centration on the intrinsic viscosity, $[\eta]$. It appears from the $[\eta]$ values that the degree of hydration increases with rising polysorbate and sorbitol concentration. Similar plots of calculated η_{red} (Table 1) vs ϕ were obtained for the other polysorbate:sorbitol mass ratios. Increasing hydration with diminishing mass ratio was apparent at a constant concentration of polysorbate and sorbitol of 40%

The data were found to fit Eqn 1 rewritten in the form:

$$\frac{\phi}{\ln \eta_{rel}} = \frac{1}{a} - \frac{K\phi}{a} \quad (2)$$

Fig. 3 shows the linear plots obtained for $\phi/\ln \eta_{rel}$ vs ϕ , for microemulsions with the studied concentrations of polysorbate and sorbitol at a mass ratio of 1:2.5. The values of a and K were derived by linear regression analysis and are listed in Table 2. The data obtained for microemulsions at the polysorbate:sorbitol mass ratios studied

TABLE 1

Reduced viscosity for microemulsions with a polysorbate 80 and sorbitol concentration of 40% by weight

Mass ratio (polysorbate:sorbitol)	Oil volume fraction (ϕ)	Reduced viscosity (η_{red})
1:1.5	0.039	4.05
	0.078	4.74
	0.118	5.79
	0.157	7.23
	0.196	9.10
1:2.0	0.039	4.35
	0.079	5.07
	0.118	6.30
	0.158	7.76
	0.197	9.97
1:2.5	0.040	4.63
	0.079	5.39
	0.119	6.53
	0.158	7.89
	0.198	9.99
1:3.0	0.040	4.75
	0.080	5.57
	0.119	6.90
	0.159	8.08
	0.199	10.04

here were treated in a similar manner and the values of a and K are also given in Table 2. k appears to decrease with diminishing polysorbate:sorbitol mass ratio. Similar results were reported for oil-in-water microemulsions by Attwood et al. (1974). Assuming that, at a given value of ϕ , the droplet size decreases with increasing concentration of surfactant and cosurfactant in the system (Baker et al., 1984b; Attwood and Ktistis, 1988), the decrease in K determined for an increase in polysorbate and sorbitol concentration conflicts with the observations of Matsumoto and Sherman [1969] but is in agreement with those of Attwood et al. (1974) and Baker et al. (1984b).

The values of a increased linearly with increase in the polysorbate and sorbitol concentration. The deviation of experimental values for a from the theoretical value for spheres of 2.5 can be attributed to droplet hydration. The ratio of bound

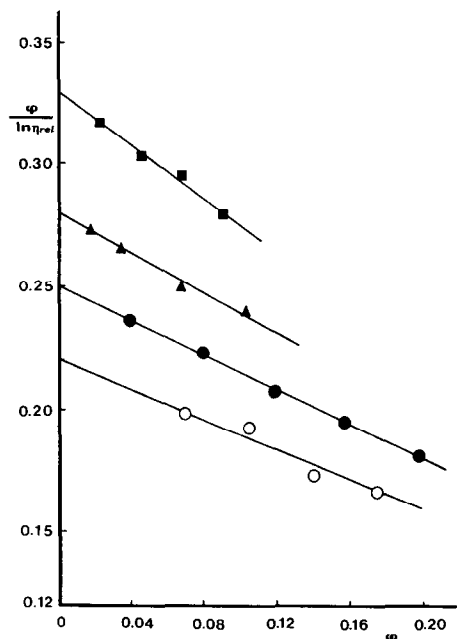


Fig. 3. Variation of $\phi/\ln \eta_{rel}$ with ϕ for microemulsions with a polysorbate:sorbitol mass ratio of 1:2.5 and polysorbate and sorbitol concentrations of (■) 30%, (▲) 35%, (●) 40% and (○) 45% w/w.

solvent layer to droplet core radius. $\Delta R/R$, can be calculated from simple geometric considerations:

$$\frac{a}{2.5} = \left(1 + \frac{\Delta R}{R}\right)^3 \quad (3)$$

where $a/2.5$ is the apparent increase in volume

TABLE 2

Values of constant a , hydrodynamic interaction coefficient K and ratios of bound solvent layer to droplet core radius, $\Delta R/R$

wt.% (polysorbate + sorbitol)	Mass ratio (polysorbate :sorbitol)	a	K	$\Delta R/R$
30	1:2.5	3.04	1.72	0.07
35	1:2.5	3.57	1.46	0.13
40	1:1.5	3.51	1.72	0.12
40	1:2.0	3.87	1.49	0.16
40	1:2.5	4.00	1.44	0.17
40	1:3.0	4.17	1.25	0.19
45	1:2.5	4.57	1.39	0.22

fraction due to the presence of a considerable quantity of solvent mechanically entrapped between the polyoxyethylene chains.

The results of the calculations are listed in Table 2 and indicate that the bound solvent layer is between 7 and 22% of the droplet core radius. The results show a linear increase in $\Delta R/R$ with increase in surfactant and cosurfactant concentration. This is consistent with the study of Attwood and Ktistis (1988) in which they reported a decrease in droplet size with increase in concentration of surfactant and cosurfactant in an oil-in-water microemulsion.

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