Rheology and Stability of Water-in-Oil-in-Water Multiple Emulsions Containing Span 83 and Tween 80

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ABSTRACT

Multiple emulsions are often stabilized using a combination of hydrophilic and hydrophobic surfactants. The ratio of these surfactants is important in achieving stable multiple emulsions. The objective of this study was to evaluate the long-term stability of water-in-oil-in-water (W/O/W) multiple emulsions with respect to the concentrations of Span 83 and Tween 80. In addition, the effect of surfactant and electrolyte concentration on emulsion bulk rheological properties was investigated. Light microscopy, creaming volume, and rheological properties were used to assess emulsion stability. It was observed that the optimal surfactant concentrations for W/O/W emulsion long-term stability were 20% wt/vol Span 83 in the oil phase and 0.1% wt/vol Tween 80 in the continuous phase. Higher concentrations of Tween 80 had a destructive effect on W/O/W emulsion stability, which correlated with the observation that interfacial film strength at the oil/water interface decreased as the Tween 80 concentration increased. High Span 83 concentrations increased the storage modulus G' (solidlike) values and hence enhanced multiple emulsion stability. However, when 30% wt/vol Span 83 was incorporated, the viscosity of the primary W/O emulsion increased considerably and the emulsion droplets lost their shape. Salt added to the inner aqueous phase exerted an osmotic pressure that caused diffusion of water into the inner aqueous phase and increased W/O/W emulsion viscosity through an increase in the volume fraction of the primary W/O emulsion. This type of viscosity increase imposed a destabilizing effect because of the likelihood of rupture of the inner and multiple droplets.

KEYWORDS

multiple emulsions, stability, rheology, surfactant

INTRODUCTION

Water-in-oil-in-water (W/O/W) multiple emulsions are emulsion systems where small water droplets are entrapped within larger oil droplets that in turn are dispersed in a continuous water phase. Because of the presence of a reservoir phase inside droplets of another phase that can be used to prolong release of active ingredients, multiple emulsions find many applications in industries such as pharmaceuticals and cosmetics.¹

Multiple W/O/W emulsions contain both W/O and O/W simple emulsions and require at least 2 emulsifiers to be present in the system when prepared using the 2-step method,² one that has a low Hydrophile-Lipophile Balance (HLB) value to stabilize the primary W/O emulsion and one that has a high HLB value to stabilize the secondary O/W emulsion.³ The low-HLB surfactant is dominantly hydrophobic and is added to the oil phase. The high-HLB surfactant is dominantly hydrophilic and is added to the outer continuous aqueous phase. The concentration ratio of these 2 surfactants is important to obtain stable and high yields of W/O/W emulsions.² There are 2 interfaces in a W/O/W multiple emulsion. The primary interface, lying between the inner aqueous phase and the oil phase, contains the low-HLB surfactant. In contrast, both the high- and the low-HLB surfactants are present at the secondary interface (between the multiple droplets and the outer continuous aqueous phase).⁴ When the hydrophilic surfactant in the continuous aqueous phase exceeds its critical micelle concentration, the resultant micelles may solubilize the hydrophobic surfactant that was originally present in the oil phase and carry it into the outer continuous aqueous phase, resulting in a decrease in the concentration of hydrophobic surfactant in the oil phase. This can eventually lead to rupture of the oil layer and loss of the internal aqueous droplets.⁵ To maintain a sufficient amount of the hydrophobic surfac-

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tant in the oil phase in order to prevent the oil layer from rupturing, a high concentration of hydrophobic surfactant is preferred. On the other hand, to avoid any potential toxicity associated with surfactants, a minimal concentration of the hydrophobic surfactant is desired in multiple emulsion preparations used pharmaceutically. Therefore, the optimal concentration of hydrophobic surfactant needs to be determined during formulation development. In this study, W/O/W multiple emulsions containing Span 83 as the low-HLB surfactant and Tween 80 as the high-HLB surfactant were prepared. The stability of these multiple emulsions as functions of Span 83 concentration in the oil phase as well as Tween 80 in the external continuous phase was evaluated.

A unique property of W/O/W multiple emulsions compared to simple W/O emulsions is the diffusion of water through the oil phase because of unbalanced osmotic pressures between the internal and external aqueous phases. The oil layer acts as a membrane separating these 2 aqueous phases. Polar molecules dissolved in either the internal aqueous phase or the external continuous aqueous phase can pass through the oil layer⁶ by diffusion because of the concentration gradient. In the case of water this is driven by osmotic pressure. Molecules are often transported via micelles of hydrophobic surfactant present in the oil phase. Water diffusion causes swelling, bursting, or shrinkage of the internal aqueous droplets, affecting the stability of the multiple droplets as well as the release profiles of the active ingredients loaded in the inner dispersed aqueous phase.⁷ The volume fraction of the primary emulsion in the multiple emulsion system is changed because of water diffusion. Change in the volume fraction of the primary emulsion alters the rheological properties of multiple emulsions.

As with simple emulsions, the manner in which multiple emulsions flow is one of their most characteristic properties. Therefore, an understanding of the rheological behavior of multiple emulsions is important in formulating, handling, mixing, processing, transporting, and storing such systems. Furthermore, rheological studies can provide useful information on the stability and internal microstructure of multiple emulsions. Although there is a substantial amount of literature published on the rheology of simple emulsions,⁸⁻¹² little attention has been given to multiple emulsions.¹³

In this study, the rheological properties of W/O/W multiple emulsions containing the surfactants Span 83 and Tween 80 were determined. The information gathered here is correlated with the long-term stability of the

W/O/W multiple emulsions to help elucidate destabilization mechanisms.

MATERIALS AND METHODS

Materials

Span 83, Tween 80, and light mineral oil were purchased from Aldrich (Milwaukee, WI). Sodium salicylate was obtained from JT Baker (Phillipsburg, NJ). Deionized water purified from a Millipore (Bedford, MA) system was used. Span 83 is a sesquiterpene of monooleate and dioleate at a 2:1 molar ratio and has an HLB of 3.7. It is commonly used in pharmaceuticals because of its low toxicity. Its structure is shown in **Figure 1**.

Figure 1. Chemical structure of Span 83.

W/O/W Preparation

Multiple emulsions, either W/O/W or O/W/O emulsions, are generally prepared using a 2-step procedure, as reported by Matsumoto et al.² For W/O/W emulsions, the primary emulsion (W/O) is first prepared using water and a low-HLB surfactant solution in oil. In the second step, the primary emulsion (W/O) is reemulsified in an aqueous solution of a high-HLB surfactant to produce a W/O/W multiple emulsion. The first step—that is, the preparation of the primary emulsion—is usually carried out in a high-shear device to produce very fine droplets. The second emulsification step is carried out in a low-shear device to avoid rupturing the multiple droplets.

In this study, the primary W/O emulsion was prepared by adding an aqueous solution containing sodium salicylate to a Span 83 solution in light mineral oil at an equal vol-

ume ratio and stirring with a magnetic mixer (1000 rpm) for 15 minutes. The concentration of Span 83 in light mineral oil varied from 0.1% to 40% wt/vol. In the second step, the W/O primary emulsion was reemulsified in a Tween 80 solution containing concentrations of Tween 80 from 0.1% to 10% wt/vol at an equal volume ratio and stirred for 5 minutes at 600 rpm to produce the W/O/W multiple emulsion.

Creaming Volume Measurement

The volumes of the creamed phase and the remaining W/O/W multiple emulsion were recorded. The creaming volume was defined in this study as the relative difference in volume of the multiple emulsion and the volume of the creamed phase. The expression used for calculation of the creaming volume is as follows:

$$V_{cream} = \frac{V_{multiple\ emulsion} - V_{creamed\ phase}}{V_{multiple\ emulsion}} \times 100\% \quad (1)$$

Microscopic Observation

An Olympus BH-2 polarized light microscope equipped with a 3CCD camera and a computer (Olympus Corporation, New Hyde Park, NY) was used to take photomicrographs. Glass microslides (3 x 1 in.) and coverslips (No. 11/2) from VWR Scientific (Plainfield, NJ) were used to prepare microscopic samples throughout the experiments. Microslides and coverslips were rinsed with the external continuous aqueous phase of the W/O/W emulsions. The W/O/W emulsion samples were then placed on a microslide with care to minimize possible destruction of emulsion structures by shear stress. The samples were covered with a coverslip and sealed using vacuum grease to prevent water evaporation. Light intensity was kept at a minimum to reduce sample heating.

Droplet Size Measurement

The information regarding the multiple droplet sizes was obtained by taking photomicrographs of the emulsion samples. The emulsions were diluted with the same continuous phase before the photomicrographs were taken.

Bulk Rheological Property Measurement

Rheological measurements were carried out using an AR 1000 rheometer (TA Instruments, New Castle, DE) with a 6-cm-diameter cone-and-plate geometry measuring system. The geometry had a 2° angle and was made of acrylic polymer. Rotational mapping was performed to eliminate possible small variations caused by the uneven surface of the shaft. A continuous ramping flow mode was used to measure viscosity under controlled shear stress ranging from 0.01 to 100 Pa. An oscillation procedure at a constant frequency of 1 Hz was used to obtain information on storage and loss moduli. Both flow and oscillatory data were collected at 25°C.

RESULTS AND DISCUSSION

Effect of Surfactant Concentration Ratio on Stability of W/O/W Multiple Emulsion

The composition of W/O/W emulsion formulations and their corresponding stabilities are given in **Table 1**. The stability of the formulations was assessed via microscopic observation of emulsion structure and measurement of creaming volume. Creaming, resulting from flocculation and concentration of emulsion droplets, is not considered a mark of instability for simple emulsions. However, flocculation and resultant creaming represent potential steps toward complete coalescence of the dispersed phase. In addition, for W/O/W multiple emulsions the creaming volume is indicative of the stability of the internal aqueous droplets entrapped in the multiple droplets, since swelling or shrinkage of the internal aqueous droplets directly affects the multiple droplet size and hence the creaming volume.

At low span concentrations (0.1% wt/vol), rapid coalescence among the inner and multiple droplets as well as loss of inner droplets to the external continuous aqueous phase occurred, resulting in phase separation within a short period of time. At 1% wt/vol of Span 83 the inner aqueous droplets were smaller compared to formulations with 0.1% wt/vol Span 83. Smaller initial droplet size provided an enhanced kinetic stability of the inner droplets to coalescence. However, the multiple droplets still coalesced rapidly, leading to the formation of W/O simple emulsions and separate oil and aqueous phases within a few weeks after preparation. When the Span 83 concentration was increased to 5% wt/vol, very fine inner aqueous droplets formed. The size of the inner droplets was estimated microscopically to be less than a micron, and the size of any droplets that were in contact was difficult to determine. The multiple droplets became smaller and their coalescence occurred less frequently than formula

Table 1. Formulation Composition of W/O/W Emulsion Formulations Containing Various Concentrations of Span 83 and Stability After 16 Months' Storage (25°C)*

Formulation	1	2	3	4	5	6	7	8	9
W ₁ phase (DI water)									
Sodium salicylate, %	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
O phase (mineral oil)									
Span 83, %	0.1	1	5	10	15	20	25	30	40
W ₂ phase (DI water)									
Tween 80, %	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Creaming volume†	100	100	68	50	36	32	23	22	23
Stability	Water and oil	Water, simple O/W, and oil	Water, W/O/W, and oil	Water, W/O/W, and oil	Water and W/O/W	Water and W/O/W	Water and W/O/W	Water and W/O/W	Water and W/O/W

*W/O/W indicates water in oil in water; DI indicates deionized.

†Calculated according to Equation 1.

tions with 0.1% wt/vol and 1.0% wt/vol Span 83. At 16 months after preparation, there were still some multiple droplets present in the formulations containing 5% wt/vol Span 83.

As the Span 83 concentration was further increased, the size of the inner droplets remained relatively unchanged, but the size of multiple droplets decreased considerably, from approximately 50 μm at 5% wt/vol Span 83 to about 10 μm at 20% wt/vol (Figure 2). These emulsions were more stable, as evidenced by lower creaming volumes and a higher percentage of multiple droplets retained after 16 months' storage at room temperature. Stability increased with an increase in Span 83 concentration within this range. However, when the Span 83 concentration reached 30% wt/vol, the primary emulsion was too viscous to be effectively dispersed in the continuous aqueous phase to form a W/O/W emulsion with spherical multiple droplets under the agitation conditions used in the secondary emulsification process. The W/O emulsion was significantly more viscous at 30% wt/vol than at 5% wt/vol, and the rheological behavior of the emulsion was non-Newtonian at 20% wt/vol or higher (Figure 3). The multiple emulsions with 30% wt/vol Span 83 are wormlike in shape (Figure 4). The average length of the multiple droplets of this formulation was a few hundred microns, as determined by microscopy.

The stability of multiple W/O/W emulsion formulations containing varying amounts of Tween 80 and a

constant concentration of Span 83 was evaluated (Table 2). It was observed that the stability of the formulations decreased as Tween 80 concentration increased. These results agree with those of Matsumoto et al.,² who suggested that high concentrations of water-soluble surfactants solubilize the oil-soluble surfactant and cause disruption of multiple droplets. Hou and Papadopoulos⁵ reported a negative synergistic effect of Tween 80 in stabilizing multiple droplets in their study of multiple emulsions containing Span 80 and Tween 80. Opawale and Burgess determined the interfacial elasticity of Span 83 and Tween 80 at the planar water/oil interface and reported that interfacial film strength decreased as Tween 80 concentration increased.⁴

Rheological Properties of W/O/W Multiple Emulsions at Different Concentrations of Surfactants and Electrolytes

To characterize the W/O/W multiple emulsions stabilized with Span 83 and Tween 80, the viscosity of these emulsion formulations was measured. The difference in the viscosity of the W/O/W multiple emulsions as a function of Span 83 concentration in the oil phase could be observed only at low shear stress because of their delicate structure (Figure 5). At a shear stress of 50 Pa or above, the multiple emulsion structure was destroyed and the viscosity of the system was reduced to that of the continuous aqueous phase.

Figure 2. Photomicrographs of freshly prepared W/O/W emulsions containing 0.5% wt/vol sodium salicylate in the inner aqueous phase, 0.1% wt/vol Tween 80 in the outer continuous aqueous phase, and various amounts of Span 83 in the oil phase (25°C). (A) 0.1% wt/vol Span 83, (B) 1.0% wt/vol Span 83, (C) 5.0% wt/vol Span 83, (D) 20% wt/vol Span 83.

Figure 3. Viscosity of freshly prepared primary W/O emulsions containing various concentrations of Span 83 in the oil phase (25°C).

Figure 4. Freshly prepared W/O/W multiple emulsion containing 0.5% wt/vol sodium salicylate in the inner aqueous phase, 0.1% wt/vol Tween 80 in the outer continuous phase, and 30% wt/vol Span 83 in the oil phase.

The viscosity of the W/O/W multiple emulsions was measured at different times following preparation (**Figure 6**). The viscosity of W/O/W multiple emulsions was shown to depend on the volume fraction of the primary W/O emulsion in the system. Water diffusion from the inner aqueous phase to the outer continuous phase or vice versa affects the volume fraction and,

therefore, changes the viscosity of the W/O/W emulsion. The relationship between the viscosity and the volume fraction is described by the Mooney equation^{14,15}:

$$\ln \eta_r = \frac{K_1 \phi_{primary}}{1 - K_2 \phi_{primary}} \quad (2)$$

where η_r is the relative viscosity of the multiple emulsion (defined as the ratio of the multiple emulsion viscosity to the external continuous phase viscosity), $\phi_{primary}$ is the volume fraction of the primary emulsion in the multiple emulsion system, and K_1 and K_2 are empirical constants dependent on droplet shape and crowdedness. Swelling of the internal aqueous droplets results in a direct increase in $\phi_{primary}$ and hence an increase in viscosity. The W/O/W emulsions in this study contain 0.5% wt/vol sodium salicylate in the inner phase and no salt in the outer continuous phase. Driven by the osmotic pressure difference, water passed from the continuous aqueous phase into the inner aqueous phase, resulting in an increase in ϕ and consequently an increase in viscosity over time. The increase in viscosity was relatively rapid and followed by a slow decrease in viscosity due to a gradual permeation of salt through the oil layer to the external continuous aqueous phase and a subsequent back diffusion of water from the inner aqueous phase to the outer aqueous phase (**Figure 7**). The slow decrease in viscosity could also result from coalescence of the inner water droplets with the external continuous water phase.

The viscosity of the W/O/W multiple emulsions after 60

Table 2. Formulation Composition of W/O/W Emulsion Formulations Containing Different Span and Stability After 16 Months' Storage (25°C)*

Formulation	3	10	11	12
W ₁ phase (DI water)				
Sodium salicylate, %	0.5	0.5	0.5	0.5
O phase (mineral oil)				
Span 83, %	5	5	5	5
W ₂ phase (DI water)				
Tween 80, %	0.1	1	5	10
Creaming volume†	68	87	95	95
Stability	Water, W/O/W, and oil	Water, simple O/W, and oil	Water, simple O/W, and oil	Water, simple O/W, and oil

*W/O/W indicates water in oil in water; DI indicates deionized

†Calculated according to Equation 1.

Figure 5. Viscosity of freshly prepared multiple W/O/W emulsions containing 0.5% wt/vol sodium salicylate in the inner dispersed aqueous phase, 0.1% wt/vol Tween 80 in the outer continuous aqueous phase, and varying amounts of Span 83 in the oil phase (25°C).

Figure 6. Non-Newtonian flow behavior of multiple W/O/W emulsions containing 0.5% wt/vol sodium salicylate in the inner aqueous phase, 0.1% wt/vol Tween 80 in the outer continuous phase, and 5% wt/vol Span 83 in the oil phase. The viscosity was measured after the W/O primary emulsions and the outer continuous phase were mixed and stirred for different times (25°C).

Figure 7. Viscosity as a function of aging time for multiple W/O/W emulsions containing 0.5% wt/vol sodium salicylate in the internal aqueous phase, 5% wt/vol Span 83 in the oil phase, and 0.1% wt/vol Tween 80 in the external continuous aqueous phase. The viscosity was measured at shear stress of 10 Pa (25°C) and relative to the viscosity of mineral oil.

minutes' aging as a function of salt concentration in the inner aqueous phase is given in **Figure 8**. It shows that the viscosity did not increase until the salt concentration reached 0.2% wt/vol. This salt level was needed to get the $\phi_{primary}$ into the region where it affects viscosity. When the salt concentration changed from 0.2% to 0.3% wt/vol, the viscosity increased significantly; this increase can be described by the Mooney equation (Equation 2). After 0.3% wt/vol of salt was added, the viscosity increase slowed and eventually leveled off because of depletion of the external continuous aqueous phase manifested as no creaming on storage.

Salt has a complex effect on the stability of W/O/W multiple emulsions. It helps counterbalance the Laplace curvature pressure on emulsion droplets when added to the inner aqueous phase, and it stabilizes the inner droplets.¹⁶ On the other hand, it causes swelling and possibly rupturing of the inner aqueous droplets because of water influx resulting from increased internal osmotic pressure. **Table 3** shows the stability of W/O/W multiple emulsions containing sodium salicylate or sodium chloride in either the internal or the external aqueous phases 1 year following preparation as previously¹⁷ reported. Formulations 3 and 14, with 0%

or 0.5% wt/vol sodium salicylate in the internal aqueous phase and no salt in the external aqueous phase, which had a moderate viscosity initially, showed good stability. Formulations 15 to 16 containing sodium salicylate or sodium chloride in the external aqueous phase but no salt in the internal aqueous phase, which had a low viscosity because of reverse osmotic pressure and shrinkage of the internal aqueous droplets, showed poor stability. Formulation 13, containing 0.5% wt/vol sodium chloride in the internal aqueous phase, which had a high viscosity initially, also showed poor stability because of subsequent rupture of the internal aqueous droplets. These findings indicated that the viscosity increase caused by salt in the inner aqueous phase had a different effect on emulsion stability than did the viscosity increase caused by the Span 83 concentration increase in the oil phase. There was an optimal value in emulsion viscosity in terms of the salt effect, whereas for the viscosity increase due to Span 83, it appeared that the higher the viscosity, the better the emulsion stability.

The stability of the multiple emulsions containing 5% wt/vol and 20% wt/vol Span 83 after 16 months' storage was compared (**Figure 9**). At 5% wt/vol Span 83, the sizes of both the multiple and inner droplets increased

Figure 8. Effect of sodium salicylate concentration in the inner aqueous phase on the viscosity of freshly prepared W/O/W multiple emulsions containing 5% wt/vol Span 83 in the oil phase and 0.1% wt/vol Tween 80 in the outer continuous phase. The viscosity was measured at a shear stress of 10 Pa (25°C) and relative to the viscosity of mineral oil.

Table 3. Stability of W/O/W Formulations Containing Salt in the Internal or External Aqueous Phase*

Formulation	3	13	14	15	16
W ₁ phase (DI water)					
Sodium chloride, %	0	0.5%	0	0	0
Sodium salicylate, %	0.5	0	0	0	0
O phase (mineral oil)					
Span 83, %	5	5	5	5	5
W ₂ phase (DI water)					
Tween 80, %	0.1	0.1	0.1	0.1	0.1
Sodium chloride, %	0	0	0	0	0.5
Sodium salicylate, %	0	0	0	0.5	0
Stability after 1 y at room temperature	Creamed W/O/W	Oil, water, and W/O/W	Creamed W/O/W	W/O	No emulsion

*W/O/W indicates water in oil in water; DI indicates deionized.

Figure 9. Photomicrographs of stability of W/O/W multiple emulsions containing 0.5% sodium salicylate in the inner aqueous phase, 0.1% wt/vol Tween 80 in the outer continuous aqueous phase, and 5% wt/vol or 20% wt/vol Span 83 in the oil phase (25°C). (A) An emulsion with 5% wt/vol Span 83, freshly prepared; (B) the same emulsion with 5% wt/vol Span 83, after 16 months' room temperature storage; (C) an emulsion with 20% wt/vol Span 83, freshly prepared; (D) the same emulsion with 20% wt/vol Span 83, after 16 months' room temperature storage.

considerably over the 16-month period compared to their initial values. At 20% wt/vol Span 83, the inner droplets increased substantially over the same period of time, but the growth of the multiple droplets was relatively small.

The smaller increase was possibly due to smaller initial multiple droplet sizes at 20% wt/vol Span 83, the increased interfacial film strength at higher surfactant concentration, or increased bulk elasticity. The loss module G'' (liquidlike) and the storage module G' (solidlike) of the W/O/W multiple emulsions containing 5% and 20% wt/vol Span 83, respectively, were measured (**Figure 10**). At 5% wt/vol Span 83 the formulation only showed some viscoelasticity at low oscillation stress and became fluid as oscillatory stress was increased to ~ 1.0 Pa. However, at 20% wt/vol the formulation was very viscoelastic or solidlike, indicated

by much higher G' values and its tolerance of much higher oscillatory stress force applied. A W/O/W multiple emulsion containing 1% wt/vol Span 83 was also tested. The G'' was higher than the G' over the entire oscillation stress range, indicating that the formulation was very fluid.

The viscosity of freshly prepared and 16-month-aged multiple W/O/W emulsion formulations containing various amounts of Span 83 is shown in **Figure 11**. After 16 months' storage, the viscosity of these formulations decreased only slightly, indicating a small net water diffusion through the oil layer during storage.

CONCLUSION

The W/O/W multiple emulsion formulation containing 20% Span 83 and 0.1% Tween 80 showed the best long-

Figure 10. Loss and storage moduli (G' and G'') vs. oscillatory stress of freshly prepared W/O/W multiple emulsions containing 0.5% wt/vol sodium salicylate in the inner aqueous phase, 0.1% Tween 80 in the outer continuous aqueous phase, and various amounts of Span 83 in the oil phase. (A) 1% wt/vol Span 83, (B) 5% wt/vol Span 83, and (C) 20% wt/vol Span 83.

term stability. After 16 months' storage at room temperature, this emulsion formulation had the most multiple droplets remaining and showed the lowest creaming volume. It was shown to be critical to minimize the Tween 80 in the continuous aqueous phase because high Tween 80 concentrations solubilize Span 83, making it unavailable to stabilize the primary emulsion. It was observed that Span 83 concentration in the oil phase significantly affected the W/O/W multiple emulsion stability. Both the inner dispersed aqueous droplets and the multiple droplets substantially reduced their sizes as Span 83 concentration in the oil phase was increased. The reduced droplet size is believed to provide an enhanced kinetic stability to coalescence in addition to lowered interfacial tension and increased interfacial film strength as a result of increased surfactant concentration.

Span 83 concentration increases the bulk elasticity of these W/O/W emulsions. The results of storage and loss moduli measurements suggest that the W/O/W emulsions with 20% wt/vol Span 83 are more elastic (solidlike) and thus more stable than those with only 5% wt/vol Span 83. This is in agreement with the interfacial elasticity data (4) indicating stronger interfacial film strength, and hence more stable W/O/W emulsions, at higher Span 83 concentrations. However, the concentration of Span 83 in the oil phase appreciably increases the viscosity of the W/O primary emulsion. When the Span 83 concentration reaches 30% wt/vol, no effective dispersion of the W/O primary emulsion in the external continuous aqueous phase is obtained.

Incorporation of salt in the internal aqueous phase increases the viscosity of W/O/W multiple emulsions because of inner droplet swelling and increased volume fraction ϕ . The swollen droplets may eventually rupture, which destabilizes emulsions. Therefore, a significant increase in viscosity due to salt addition to the internal aqueous phase is an indication of the poor long-term stability of W/O/W emulsions.

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Figure 11. Viscosity of freshly prepared and 16-month-aged W/O/W multiple emulsions containing 0.5% wt/vol sodium salicylate in the inner aqueous phase, 5% wt/vol Span 83 in the oil phase, and 0.1% Tween 80 in the outer continuous aqueous phase. Viscosity values were measured at shear stress of 10 Pa (25°C) and relative to the viscosity of mineral oil.

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