Effect of methylcellulose on the stability of oil-in-water emulsions

Rampurna P. Gullapalli[a], Bhogi B. Sheth[b],*

[a]*R.P. Scherer North America, 2725 Scherer Drive, St. Petersburg, FL 33716, USA*
[b]*Parenteral Medications Laboratories, Department of Pharmaceutical Sciences, College of Pharmacy, 62 South Dunlap, University of Tennessee, Memphis, TN 38163, USA*

Abstract

The objective of this study was to investigate how polymers used as auxiliary emulsifiers improve the stability of oil-in-water emulsions. One stable emulsion and three unstable emulsions were formulated with 30% mineral oil and an emulsifier blend of Tween® 40 and Span® 20. The stable emulsion (SE) contained 2% emulsifier blend optimized for maximum stability. One unstable emulsion, UE1, was formulated to contain 0.5% of the same emulsifier blend as the SE formulation. Two unstable emulsions were formulated to contain an unbalanced emulsifier blend, one with excessive hydrophilic emulsifier (UE2) and one with excessive lipophilic emulsifier (UE3). A series of emulsions was prepared containing increasing amounts of methylcellulose for each base emulsion. Creaming and change in particle size were measured to evaluate stability. The addition of the polymer to the stable emulsion caused instability leading to creaming and eventual oil separation. This effect of the polymer was more pronounced in UE1 emulsions. However, the addition of the polymer improved the stability of the UE2 and UE3 series of emulsions. The polymer also caused a reduction in the particle size of UE3 emulsions and a proportionally larger increase in the viscosity of UE2 emulsions. These results suggest that (i) methylcellulose could act as a hydrophilic emulsifier only in the absence of Tween® 40, (ii) methylcellulose and Tween® 40 associate to form a complex and (iii) the concentration of Tween® 40 is the determining factor for the stability of emulsions. A model of the methylcellulose-Tween® 40 association and its effect at the mineral oil-water interface is proposed.

Keywords: Emulsions; Stability; Auxiliary emulsifiers; Methylcellulose; Interactions

* Corresponding author.

1. Introduction

Synthetic and natural polymers have been used as auxiliary emulsifiers to improve the physical stability of food, cosmetic and pharmaceutical emulsions (Reiger, 1986; Friberg et al., 1988). Auxiliary emulsifiers used for this purpose are usually water soluble and are thought to stabilize emulsions by either (i) modification of the rheological properties of the bulk phase (Zatz and Ip, 1986), (ii) adsorption at the oil-water interface, thereby providing a steric or an electrosteric barrier (Tadros, 1976; Bohm and Lyklema, 1976; Lankveld and Lyklema, 1972), or (iii) a combination of the two effects. A review of literature revealed that the effect of auxiliary emulsifiers was investigated on emulsion systems that were selected arbitrarily. Mechanisms for the effect of auxiliary emulsifiers were proposed based on each of the emulsion system investigated. Mechanisms proposed to explain the role of auxiliary emulsifiers from these investigations were often not clear. Studies by Oza and Frank (1986) on the effect of Tween[®] 80 on mineral oil-in-water emulsions stabilized with microcrystalline cellulose indicated that incorporation of Tween[®] into an emulsion stabilized with cellulose would have an adverse effect on the stability of emulsion. This effect was attributed to loss of cellulose structure in the continuous phase. In contrast to these adverse effects on emulsion stability, Zatz and Ip (1986) reported that the stability of mineral oil-in-water emulsions containing nonionic Oleth 3 and Oleth 10 was improved with the addition of methylcellulose, carboxymethylcellulose and xanthan. The authors attributed the stabilizing effect of these polymers to bulk phase rheology.

Bergenstahl (1988) investigated the effect of various polymers on the stability and flocculation behavior of soybean oil-in-water emulsions stabilized with conventional low molecular weight emulsifiers. He proposed that the improvement in the stability of emulsions in the presence of these polymers was due to the formation of a combined structure of a highly surface active primary surfactant layer covered by an adsorbed less surface active polymer layer at the oil-water interface. In contrast, Dickenson and Galazka (1991) reported that the nature of the interfacial film formed between highly surface active sodium caseinate and moderately surface active gum arabic at n-hexadecane-water interface was affected by competition between macromolecular components for adsorption at the interface during the emulsification process.

It was of interest to carry out a systematic investigation to understand the role of methylcellulose, as a model auxiliary emulsifier in oil-in-water emulsions stabilized with conventional low molecular weight nonionic emulsifiers. One stable and three unstable base emulsions containing 30% mineral oil were formulated using Tween[®] 40 and Span[®] 20 as the emulsifiers. A stable emulsion (SE) was formulated to contain the optimized emulsifier system. Unstable emulsions were formulated to induce instability in SE emulsion by three different methods. One unstable emulsion (UE1) was formulated to contain the optimized emulsifier system at a lower concentration. The second unstable emulsion (UE2) was formulated with the emulsifier system unbalanced to contain excessive hydrophilic emulsifier (Tween[®] 40). The third unstable emulsion (UE3) was formulated to contain excessive lipophilic emulsifier (Span[®] 20). A series of emulsions was prepared for each base emulsion containing increasing amounts of methylcellulose. Stability of emulsions was evaluated on the basis of creaming and change in particle size of the disperse phase with time. Mineral oil was chosen as the disperse phase in order to avoid any possible complications from surface active lipids, such as free fatty acids and monoglycerides present in vegetable oils. Nonionic polymers and emulsifiers were selected as they were known not to interact or to interact only weakly with other formulation components.

2. Materials and methods

2.1. Materials

Light mineral oil NF was obtained from Mallinckrodt Inc. Methylcellulose 4000 and methylcellulose 400 (Methocel[®] Premium Grade) were obtained from Dow Chemical Co. Polysor-

bate 80 NF (Tween® 80), Polysorbate 40 NF (Tween® 40), Polysorbate 20 NF (Tween® 20), sorbitan monooleate NF (Span® 80), sorbitan monopalmitate NF (Span® 40), sorbitan mono-laurate NF (Span® 20) were obtained from Emulsion Engineering Inc. Methylparaben USP from Sigma and propylparaben from Eastman Kodak Co. were used as preservatives. All the materials were used as received.

2.2. Methods

2.2.1. Selection of emulsion formulations

The emulsifier blend for the base SE formulation was optimized for maximum stability using the HLB method (Atlas HLB System, 1963). A series of Tween® and Span® type emulsifiers was screened to determine the required HLB, chemical type and concentration of the emulsifier blend for the preparation of the most stable mineral oil-in-water emulsion. Emulsions were prepared by adding the oil phase containing emulsifiers at 70°C to the aqueous phase containing preservatives, also at 70°C, with propeller mixing. Stability was evaluated after 24 h by measuring creaming volume and particle size. A 2% emulsifier blend of Tween® 40 and Span® 20 at HLB 10 was found to be optimum for the preparation of the base SE. One base unstable emulsion (UE1) was formulated to contain 0.5% of the same emulsifier blend as the SE formulation. A series of emulsions was prepared with the optimized emulsifier blend at HLB values ranging from 8.6 to 14 to select two other unstable emulsions with an excessive hydrophilic emulsifier (UE2) and with an excessive lipophilic emulsifier (UE3). These unstable formulations were selected based on their significantly larger particle sizes and lower creaming volumes than that of the base SE formulation.

2.2.2. Process optimization

Studies were carried out to evaluate the effect of the order of addition of emulsifiers and the type and degree of mixing on the stability of SE formulation. Three methods of addition of emulsifiers were investigated. In Method A, both emulsifiers were added to the oil phase. In Method B, both emulsifiers were added to the

water phase. In Method C, the hydrophilic emulsifier (Tween® 40) was added to the water phase and the lipophilic emulsifier (Span® 20) was added to the oil phase. To determine the degree of mixing required, base SE formulation was first prepared using a propeller mixer (IKA WERK Inc.) at 2000 rpm for 5, 10 and 15 min to obtain a coarse emulsion. The coarse emulsion was then homogenized (OMNI™ 2000, OMNI International Inc.) at 25 000 rpm for 5 and 10 min.

Two methods of addition of the polymer were evaluated to study the effect on the particle size of the formulations. In Method I, emulsions were prepared by adding the oil phase containing the emulsifiers at 70°C to the polymer dispersion in the water phase at 70°C. In Method II, a concentrated oil-in-water emulsion containing 50% oil phase and 50% water phase was prepared and diluted with prehydrated polymer solution to give the required polymer concentration in the external phase.

2.2.3. Preparation of emulsions

Based on the results from the above studies, Method I, described below was used for the preparation of emulsions: the polymer was dispersed in the water phase containing 0.18% w/w methylparaben and 0.02% w/w propylparaben at 90°C. The oil phase containing emulsifiers was heated to 70°C and added to the water phase at 70°C while stirring with a propeller mixer at 2000 rpm. Stirring was continued for 5 min. The emulsion container was placed in a water bath at 13°C ($\pm$ 1°C) and the coarse emulsion was further homogenized for 5 min at 25 000 rpm. Additional water was added as necessary to make up for water lost due to evaporation. The emulsion was homogenized for 1 min. Each base emulsion was prepared with 0, 0.29, 0.59, 0.88, 1.18 and 1.47% w/w polymer in the external phase.

2.2.4. Measurement of emulsion stability

Creaming and change in particle size of the disperse phase droplets with time were measured to evaluate the stability of emulsions. The creaming profiles of the emulsions were evaluated at ambient temperature using the procedure described by Zatz and Ip (1986).

Particle size distributions of emulsions were determined by the centrifugal sedimentation method using a HORIBA™ CAPA-700 particle size analyzer (HORIBA Instruments Inc.). The instrument is based on the principle of liquid-phase sedimentation with measurements being done using an optical transmission method. The instrument was calibrated using standard polystyrene divinylbenzene beads and optical microscopy. The emulsion sample was mixed in order to obtain a homogeneous sample for particle size measurement. Approximately five drops of emulsion were diluted with approximately 30 ml of distilled water. Particle size was measured immediately after dilution. Triplicate measurements were made and an average median D_{vol} was determined. The particle size was measured initially and after 2, 4 and 6 months to evaluate stability.

In addition, the degree of flocculation and size distributions were evaluated using an optical microscope (WILD™ M21, Heerbrugg, Inc.) equipped with a calibrated eyepiece micrometer and a photomicrographic attachment. Particle size distributions determined from the instrumental and microscopic methods were found to be in agreement.

2.2.5. Measurement of flow properties

Flow properties of emulsions and polymer solutions were evaluated by measuring rheograms using a Ferranti-Shirley™ Cone and Plate viscometer equipped with a hood and trough accessory (Ferranti-Shirley Electric Inc.). Rheograms were measured at 25°C using a cone with a 7 cm diameter and a 0.006 radian cone angle. A maximum shear rate of 5500 s^{-1} and a sweep time of 240 s were selected for the measurement of rheograms. The viscometer was calibrated using two viscosity standards certified to be 47.8 and 483 cps at 25°C. The rheograms were evaluated by the application of the structure equation (Niebergall et al., 1971), shown below.

$$F = f + \eta_\infty \times S - b_v \times e^{-aS}$$

Where F, dynes cm^{-2}, is the shear stress; S, s^{-1}, is the shear rate; η_∞, poise, is the viscosity at high rates of shear; f, dynes cm^{-2}, is the intercept on the stress axis obtained by extrapolation of the

linear portion of the curve; b_v, dynes cm^{-2}, is the viscoelastic constant and a is a constant. A value of 0.001 for a was found to give a good fit for all emulsion formulations and polymer solutions. The parameters, f, η_∞ and b_v were determined by fitting the ordered pairs of rate of shear and shear stress data to the structure equation using a SigmaPlot™ program. Triplicate measurements were made on each sample.

3. Results and discussion

3.1. Selection of emulsion formulations and process

The effect of HLB of 2% emulsifier blend consisting of Tween® 40 and Span® 20 on the percent creaming volume and particle size of emulsions is shown in Fig. 1. The particle size of emulsions from HLB 9 to 13 was essentially similar. However, the base SE formulation with HLB 10 showed the highest creaming volume. There was a rapid decrease in creaming volume at higher and lower HLB values. The formulations at HLB 14 and 8.6 were chosen as the two unstable emulsions with excessive hydrophilic emulsifier (UE2) and with excessive lipophilic emulsifier (UE3), respectively. Another base unstable emulsion (UE1) was formulated to contain 0.5% of the same emulsifier blend as the SE formulation.
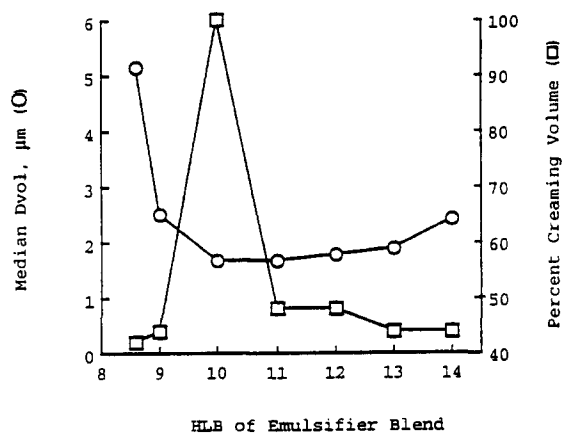

Fig. 1. Effect of HLB of emulsifier blend of Span® 20 and Tween® 40 on stability of mineral oil emulsions.

Table 1
Formulations of base mineral oil emulsions

Ingredients	Emulsion formulations			
	SE	UE1	UE2	UE3
	Concentration, %w/w			
Mineral oil	30	30	30	30
Water phase	68	69.5	68	68
Tween® 40	0.4	0.1	1.54	0
Span® 20	1.6	0.4	0.46	2
HLB	10	10	14	8.6

SE, stable emulsion.
UE1, emulsion with reduced emulsifier concentration.
UE2, emulsion with excessive hydrophilic emulsifier.
UE3, emulsion with excessive lipophilic emulsifier.

These three unstable formulations were selected based on their significantly larger particle size and smaller percent creaming volume. The formulations of base emulsions selected for the study are shown in Table 1.

A mixing time of 5 min using a propeller mixer at 2000 rpm was selected for the preparation of a coarse emulsion since there was no further reduction of particle size after 5 min. A further mixing with Omni™ homogenizer for 5 min at 25 000 rpm was found to be sufficient to produce emulsions with smaller particle size. The effect of the order of addition of the emulsifiers on the particle size of the base SE formulation was found to be insignificant. However, the creaming stability of emulsions was better when both the emulsifiers were initially added to the oil phase (Method A). The particle size of UE1 and UE3 formulations was found to be dependent on the method of addition of the polymer. As shown in Fig. 2, the particle size of emulsions was smaller when the polymer was added to the hot water phase before mixing with the oil phase (Method I).

3.2. Effect of methylcellulose on particle size

The effect of methylcellulose addition on the initial particle size distributions of emulsions formulated under various emulsifier conditions is presented in Table 2. The addition of the polymer caused a substantial reduction and narrowing of

the particle size distribution of UE3 emulsions, formulated to contain only a lipophilic emulsifier (Span® 20). The particle size reduced proportionally from 5.15 μm (± 2.3 μm) to 1.75 μm (± 1.1 μm) when methylcellulose 4000 concentration was increased from 0 to 1.47% in the external phase. A similar trend in the reduction of the particle size distributions of UE3 formulation was observed with the polymer of a lower molecular weight (methylcellulose 400). However, the addition of the polymer did not have a similar size reduction effect on SE, UE1 and UE2 formulations. This suggests that the polymer could act as a hydrophilic emulsifier in mineral oil-in-water emulsions only in the absence of a conventional hydrophilic emulsifier.

3.3. Effect of methylcellulose on flow properties

Newtonian flow was observed for 0.29% methylcellulose 4000 solution and for emulsions without the polymer and with 0.29% polymer concentration in the external phase. Rheograms of emulsions and the polymer solutions were pseudoplastic at higher polymer concentrations. Emulsions and the polymer solutions showed es-
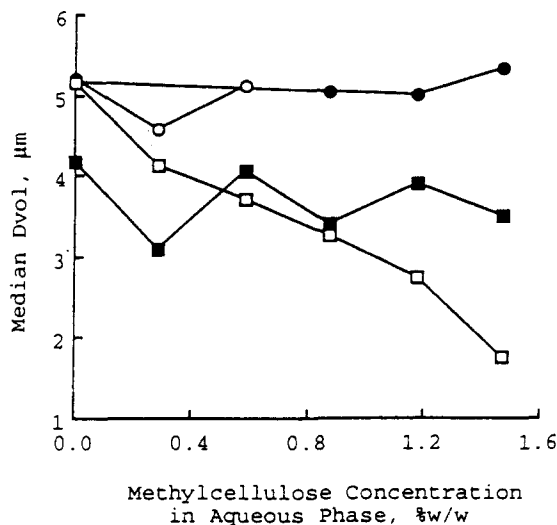

Fig. 2. Effect of method of methylcellulose 4000 addition on particle size of UE1 and UE3 emulsions. □, UE3 (Method I); ○, UE3 (Method II); ■, UE1 (Method I) and; ●, UE1 (Method II).

Table 2
Effect of methylcellulose on initial particle size of mineral oil emulsions

Concentration of Methylcellulose in external phase %w/w	Median d_{vol}^a, μm				
	Emulsion formulations				
	SE	UE1	UE2	UE3	Polymer[b]
Methylcellulose 4000					
0.00	1.97 (1.6)	4.18 (1.9)	2.42 (1.7)	5.15 (2.3)	
0.29	1.48 (1.3)	3.10 (1.3)	2.66 (1.3)	4.12 (1.5)	23.74 (7.6)
0.59	1.70 (1.3)	4.06 (1.3)	2.38 (1.3)	3.86 (1.7)	21.77 (5.9)
0.88	1.84 (1.3)	3.40 (1.3)	2.75 (1.4)	3.26 (1.4)	21.19 (5.7)
1.18	1.58 (1.3)	3.89 (1.3)	3.00 (1.2)	2.74 (1.1)	20.84 (5.3)
1.47	1.60 (1.3)	3.48 (1.3)	2.73 (1.3)	1.75 (1.1)	20.16 (5.8)
Methylcellulose 400					
0.00	1.97 (1.4)	3.75 (2.6)	2.47 (1.7)	5.15 (2.3)	
0.29	1.25 (1.1)	2.75 (1.8)	2.18 (1.3)	4.19 (1.6)	
0.59	1.35 (1.2)	2.47 (1.5)	2.42 (1.3)	4.00 (1.7)	
0.88	1.20 (0.9)	2.61 (2.0)	2.54 (1.4)	3.66 (1.6)	
1.18	1.23 (0.9)	2.54 (1.9)	2.18 (1.2)	2.54 (1.2)	
1.47	1.15 (0.9)	2.79 (2.8)	2.03 (1.3)	2.48 (1.1)	

SE, stable emulsion.
UE1, emulsion with reduced emulsifier concentration.
UE2, emulsion with excessive hydrophilic emulsifier.
UE3, emulsion with excessive lipophilic emulsifier.
[a] Mean of three measurements (SD).
[b] Emulsions with no emulsifiers.

sentially no yield value and thixotropy. The effect of viscosity of external phase on viscosity of emulsions is shown in Fig. 3. The value of η_∞ was higher for emulsions with a higher polymer concentration as might be expected. The increase in η_∞ of emulsions was directly proportional to η_∞ of the polymer solutions containing the same concentration as in the emulsions. The slopes of the linear relationship between η_∞ of emulsions and of the polymer solutions were compared among the four types of emulsions using regression analysis (Table 3). The increase in η_∞ value of UE2 emulsions, formulated to contain an excessive hydrophilic emulsifier, was significantly higher than those of SE, UE1 and UE3 emulsions ($P < 0.005$). However, no significant difference was found among the slopes of SE, UE1 and UE3 emulsions.

Higher η_∞ values of emulsions with a higher hydrophilic emulsifier (Tween® 40) concentration suggests an interaction between the polymer and the emulsifier in these formulations. The interaction between the polymer and the hydrophilic emulsifier was further confirmed by the finding that the polymer solutions with 1.54% Tween® 40 showed a higher viscosity than the corresponding solutions without Tween® 40 at polymer concentrations 1.18 and 1.47% (Fig. 4). In the present study, an increase in viscosity of emulsions and of methylcellulose solutions with a higher Tween® concentration was thought to be due to an interaction between the polyoxyethylene portion of Tween® 40 and methylcellulose. A similar mechanism of interaction between polyethylene glycols (hydrophilic portion of Tween®) and a cellulose polymer was also proposed by Storz et al. (1965) from their dialysis and rheological investigations. Our findings and those reported by Storz et al. suggest that the interactions are dependent on the concentration of both the polymer and the hy-
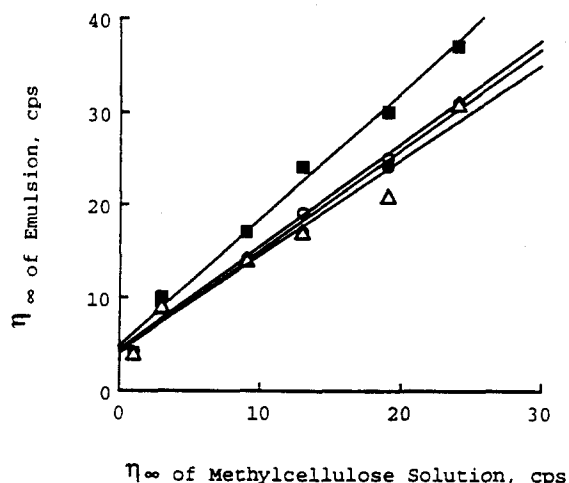
Fig. 3. Plot of η_{∞} of Methylcellulose 4000 solutions versus η_{∞} of mineral oil emulsions. ○, SE; ●, UE1; ■, UE2; and △, UE3.

drophilic emulsifier. The interactive forces between the polymer and the emulsifier appear to be stable under hydrodynamic forces generated by the applied shear during rheological measurements. Such shear resistant interactive forces between nonionic hydrophilic polymers and Tween® type emulsifiers were also reported by others (Reichman and Garti, 1988).

3.4. Effect of methylcellulose on emulsion stability

The composition of the emulsifier system had a significant effect on the creaming behavior of

Table 3
Linear regression analysis of relationship between η_{∞} of methylcellulose 4000 solutions and of mineral oil emulsions

Emulsion formulations	Slope	r^2	P-value
SE	18.24	0.998	0.3497
UE1	17.75	0.986	0.5432
UE2	22.50	0.999	0.0011
UE3	16.87	0.965	[a]

SE, stable emulsion.
UE1, emulsion with reduced emulsifier concentration.
UE2, emulsion with excessive hydrophilic emulsifier.
UE3, emulsion with excessive lipophilic emulsifier.
[a] Reference slope; statistical significance defined at a P-value ≤0.05.

emulsions containing methylcellulose. The SE formulation was destabilized on addition of the polymer, eventually leading to oil separation in emulsions with 1.18% or more of the polymer in the external phase (Fig. 5). The destabilization occurred despite the fact that the emulsifier system for the base SE formulation was optimized for maximum stability. The destabilization effect occurred in a shorter period of time and at a lower polymer concentration of 0.88% in UE1 formulation containing the same emulsifier system at a lower concentration. However, the addition of the polymer improved the creaming stability of UE2 and UE3 emulsions (UE3 > UE2) formulated with an emulsifier system unbalanced to contain an excess of either hydrophilic or lipophilic emulsifier. (Table 4). In addition, the particle size distributions of UE2 and UE3 formulations remained essentially unchanged for more than 6 months. These results suggest that the particle size stability was maintained in UE2 and UE3 emulsions even after creaming.

The base emulsion formulations without the polymer showed no creaming for one day or more depending on the formulation. Upon standing, these emulsions separated into two phases, a relatively opaque emulsion phase accumulated at the upper portion (*creamed emulsion phase*) and a dilute emulsion phase accumulated at the lower portion (*separated external phase*) of the graduated cylinder. The volumes of the two phases remained essentially constant with time. On addition of the polymer, the emulsions separated initially into two phases. The boundary between the two phases moved upward slowly with time, reducing the volume of the upper emulsion phase gradually from 100% and increasing the volume of the lower emulsion phase from 0%. The volumes of the two phases reached a steady state with time. The volume of the '*creamed emulsion phase*' at the steady state was designated the '*equilibrium creaming volume*', V_c (Table 4). The appearance of the lower phase changed from opaque to translucent to transparent with increasing polymer concentration, suggesting progressive increase in flocculation (Fig. 5). The flocculation of the emulsion droplets in the presence of the polymer was further confirmed by microscopic
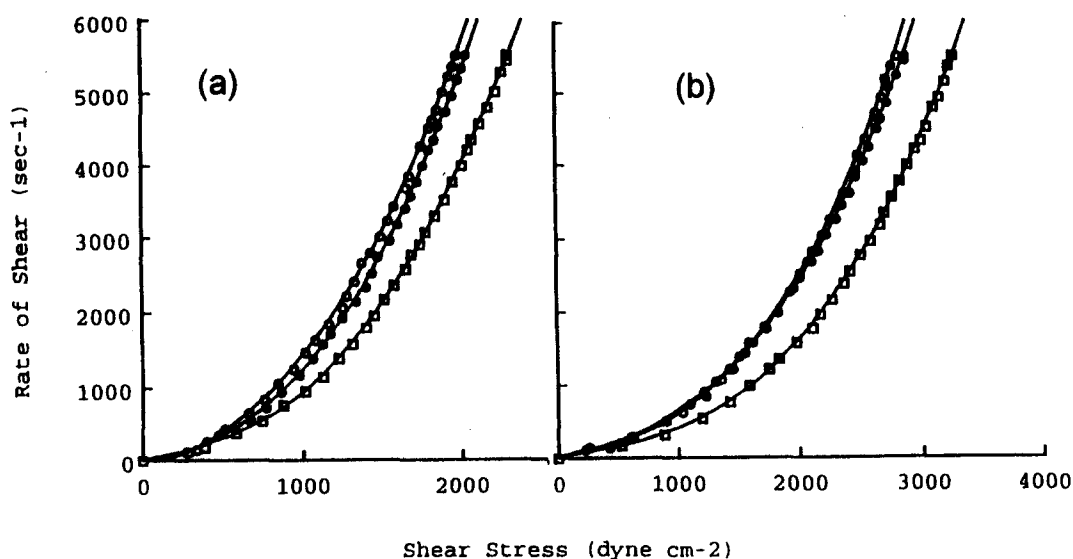
Fig. 4. Effect of Tween® 40 concentration on viscosity of (a) 1.18% and (b) 1.47% methylcellulose 4000 solutions, Tween® 40 concentration: ○, 0%; ●, 0.4%; and □, 1.54%.

examination of emulsion samples. Interestingly, the amount of polymer needed to obtain a transparent separated external phase was dependent on the hydrophilic emulsifier concentration in emulsions. The transparent external phase due to added polymer was observed at polymer concentration of 0.59% for UE2, 0.88% for SE, 1.18% for UE1 and 1.47% for UE3 emulsions. These results suggest that the hydrophilic emulsifier promotes the polymer induced flocculation in the emulsions.

The creaming curves of UE2 emulsions are shown in Fig. 6 to illustrate the typical creaming behavior of emulsions. Creaming curves of emulsions containing the polymer were linear during the first week. Therefore, an 'initial creaming rate', K_i, was calculated from the slope of this linear portion of the curve. The K_i value was lower for emulsions with a higher concentration of the polymer as might be expected due to increased viscosity of the external phase (Table 5). The K_i values of emulsions with excessive hydrophilic emulsifier (UE2) were higher than those of SE, UE1 and UE3 formulations at 0.59% and higher polymer concentrations, further confirming the notion that the hy-

drophilic emulsifier promotes the polymer induced flocculation in the emulsions.

3.5. Effect of method of methylcellulose addition on emulsion stability

The properties and stability of emulsions were known to be sensitive to manufacturing procedure (Becher, 1965; Lashmar and Beesley, 1993). To investigate the effect of method of polymer addition on stability, emulsions were prepared by an alternate method (Method II), described in Section 2.2.2. UE1 formulation was selected since the effect of the polymer could be studied in a shorter time. Four UE1 emulsions containing 0, 0.88, 1.18 and 1.47% of methylcellulose 4000 in the external phase were prepared from a concentrated emulsion. As shown in Table 6, the initial particle size distributions of the emulsions were essentially similar within each method. However, emulsions showed a slightly larger size with Method II than those prepared with Method I. Base UE1 emulsion without the polymer did not show any instability as indicated by oil separation. However, emulsions prepared using the two methods showed oil separation at polymer concentrations of 0.88% and higher. These results suggest that
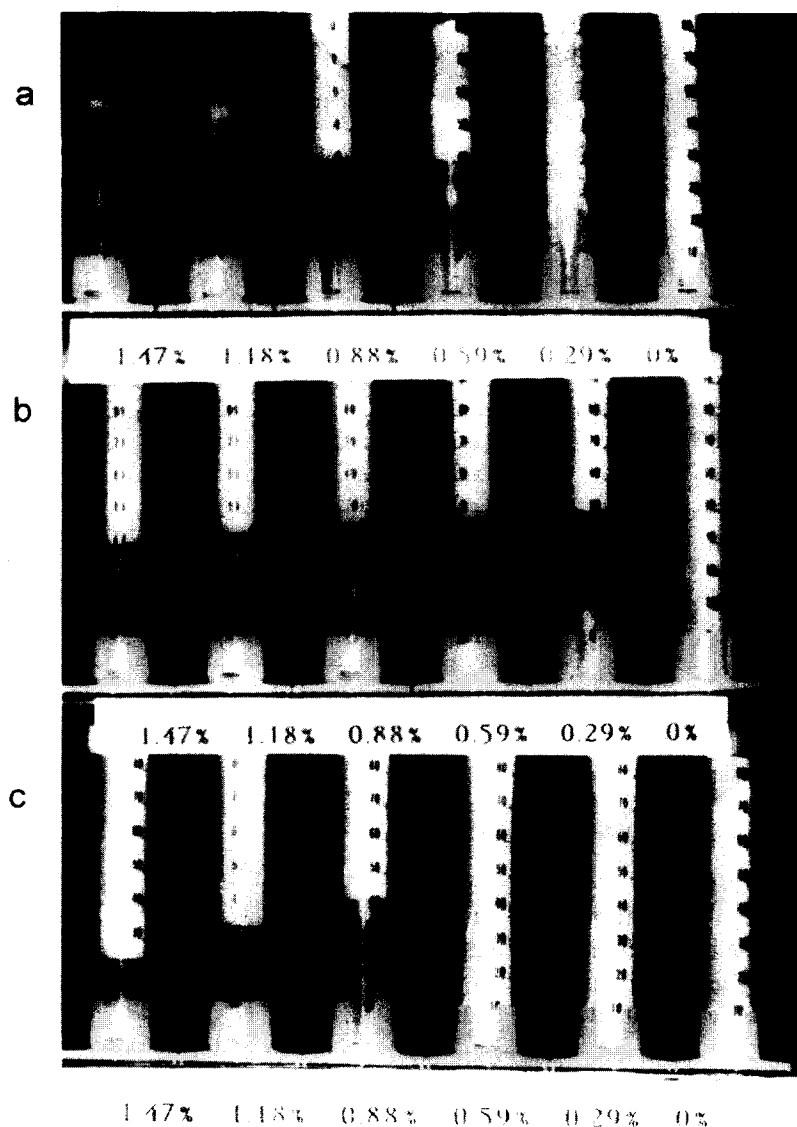
Fig. 5. Effect of methylcellulose 4000 on stability of mineral oil emulsions: a, SE; b, UE2 and; c, UE3.

the instability in these emulsions is due to the added polymer and is independent of method of polymer addition.

3.6. Effect of type of Tween® on emulsion stability

Another parameter examined was the effect of fatty acid chain length of the hydrophilic emulsifier on the emulsion stability in the presence

of the polymer. Six UE1 emulsions containing 0–1.47% of methylcellulose 4000 in the external phase were prepared at HLB 10 with Span® 20 and Tween® of varying fatty acid chain length using Method I. As shown in Table 7, the initial particle size distributions of the three emulsions were essentially similar. UE1 emulsions at lower polymer concentrations did not show any instability as indicated by oil separation. However, emulsions prepared with higher polymer

Table 4
Effect of methylcellulose on percent equilibrium creaming volume, V_e, of mineral oil emulsions

Concentration of methylcellulose in external phase %w/w	Percent equilibrium creaming volume, V_e^a				
	Emulsion formulations				
	SE	UE1	UE2	UE3	Polymer[b]
Methylcellulose 4000					
0.00	53	45	45	43	
0.29	50	49	46	42	OS
0.59	52	50	49	48	OS
0.88	58	OS	50	52	OS
1.18	OS	OS	50	57	OS
1.47	OS	OS	52	64	OS
Methylcellulose 400					
0.00	49	42	44	42	
0.29	52	41	44	42	OS
0.59	51	46	47	46	OS
0.88	53	OS	47	51	OS
1.18	OS	OS	49	55	OS
1.47	OS	OS	53	62	OS

SE, stable emulsion.
UE1, emulsion with reduced emulsifier concentration.
UE2, emulsion with excessive hydrophilic emulsifier.
UE3, emulsion with excessive lipophilic emulsifier.
OS, oil separation.
[a] Measurements were done after six months.
[b] Emulsions with no emulsifiers.

concentrations showed oil separation in all three cases, suggesting that the instability in these emulsions was due to the added polymer and was independent of type of Tween® used in the emulsions.

The effect of methylcellulose on the stability of emulsions is presented in Fig. 7. The complex effects of methylcellulose on the stability of emulsions is thought to be due to an interaction between the polymer and the hydrophilic emulsifier. In UE3 formulation with no Tween® 40, methylcellulose could act like a protective colloid with some penetration of the polymer through the emulsifier layer at mineral oil-water interface. This mechanism is helpful in explaining the reduction of particle size of these emulsions in the presence of the polymer. The multi layer interfacial barrier formed with methylcellulose and Span® 20 was firm enough to prevent coalescence of oil droplets and improve the stability of these
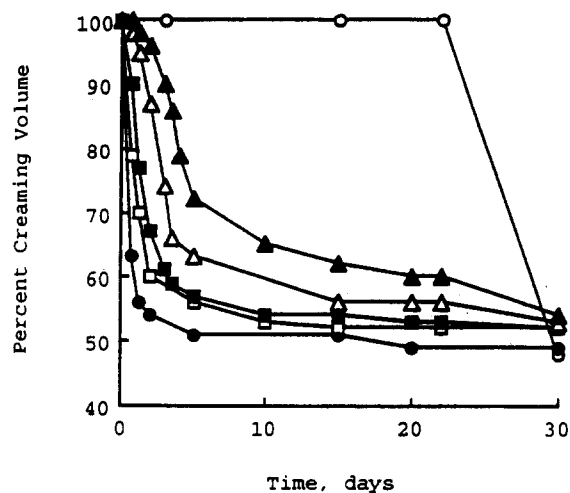

Fig. 6. Effect of methylcellulose 4000 concentration on creaming pattern of UE2 emulsions. Methylcellulose 4000 concentration in external phase: ○, 0%; ●, 0.29%; □, 0.59%; ■, 0.88%; △, 1.18% and; ▲, 1.47%.

Table 5
Effect of methylcellulose 4000 on initial creaming rate, K_i, of mineral oil emulsions

Concentration of methylcellulose in external phase %w/w	Initial creaming rate, K_i, ml%/day			
	Emulsion formulations			
	SE	UE1	UE2	UE3
0.29	13	37	34	36
0.59	13	26	28	22
0.88	9	10	19	6
1.18	3	6	10	2
1.47	<1	3	7	1

SE, stable emulsion.
UE1, emulsion with reduced emulsifier concentration.
UE2, emulsion with excessive hydrophilic emulsifier.
UE3, emulsion with excessive lipophilic emulsifier.

emulsions. In SE and UE1 formulations with a lower Tween® concentration, most of Tween® might be in the form of the methylcellulose-Tween® complex. The complex might concentrate at the oil-water interface in these systems during the emulsification process. In such a case, the particle size of these emulsions with methylcellulose remained essentially the same as of the emulsions with no methylcellulose. However, due to the hydrophilic nature of the complex and the less interaction between the polyoxyethylene chain of Tween® and the nonpolar mineral oil (Shinoda et al., 1971), the complex might possibly be dislodged from the mineral oil-water interface with time. This results in rupture of interfacial film and the subse-

quent destabilization of emulsions. In UE2 formulation with a higher Tween® concentration, some of excessive Tween® might complex with methylcellulose leaving most of Tween® in free form. The more interfacially active free Tween® could compete with less active methylcellulose-Tween® complex at the oil-water interface. Tween® would be retained at the interface, without affecting the stability of these emulsions with time.

4. Conclusions

It was concluded that the major effect of methylcellulose on the emulsion systems under investiga-

Table 6
Effect of method of methylcellulose 4000 addition on stability of mineral oil emulsions with reduced emulsifier concentration (UE1)

Concentration of methylcellulose in external phase %w/w	Method I		Method II	
	Particle[a] size	V_e	Particle[a] size	V_e
0.00	4.18 (1.9)	45	5.15 (2.3)	42
0.88	3.40 (1.3)	OS	5.03 (2.4)	OS
1.18	3.89 (1.3)	OS	5.00 (2.3)	OS
1.47	3.48 (1.3)	OS	5.32 (2.2)	OS

Method I, oil phase at 70°C added to polymer dispersion at 70°C.
Method II, a concentrated emulsion diluted with prehydrated polymer solution.
OS, oil separation.
V_e, percent equilibrium creaming volume measured after 6 months.
[a] Mean of three measurements (SD), measured initially.

Table 7
Effect of methylcellulose 4000 and hydrophilic emulsifier type on stability of mineral oil emulsions with reduced emulsifier concentration (UE1)

Concentration of Methylcellulose in external phase %w/w	Tween® 80:Span® 20[a]		Tween® 40:Span® 20[a]		Tween® 20:Span® 20[a]	
	Particle[b] size	V_e	Particle[b] size	V_e	Particle[b] size	V_e
0.00	4.12 (2.5)	44	4.18 (1.9)	45	5.20 (3.0)	45
0.29	2.69 (1.8)	44	3.10 (1.3)	49	4.69 (2.1)	46
0.59	3.02 (1.7)	49	4.06 (1.3)	50	5.19 (2.0)	46
0.88	2.82 (1.7)	52	3.40 (1.3)	OS	4.24 (1.9)	48
1.18	2.80 (1.8)	OS	3.89 (1.3)	OS	4.08 (1.8)	OS
1.47	2.97 (1.8)	OS	3.48 (1.3)	OS	4.07 (1.8)	OS

V_e, percent equilibrium creaming volume measured after six months.
OS, oil separation.
[a] Emulsions made at HLB 10.
[b] Mean of three measurements (SD), measured initially.

tion was at the mineral oil-water interface. Viscosity was a minor contributing factor in the improvement of emulsion stability. In the absence of the polymer, the emulsifier system for maximum stability was found to be an emulsifier blend with an HLB value of 10. When the polymer was present, emulsifier blends at HLB 8.7 and 14 were found to give more stable emulsions than the emulsifier blend at HLB 10. The addition of the polymer resulted in an interaction between the polymer and the hydrophilic emulsifier, causing a change in the interfacial film stabilizing the emulsion. This would change the emulsifier requirements as determined by methods such as the HLB and the PIT (phase inversion temperature) system. Therefore, HLB studies for the selection of an appropriate emulsifier system should be done with emulsions containing the polymer to be used as the auxiliary emulsifier.
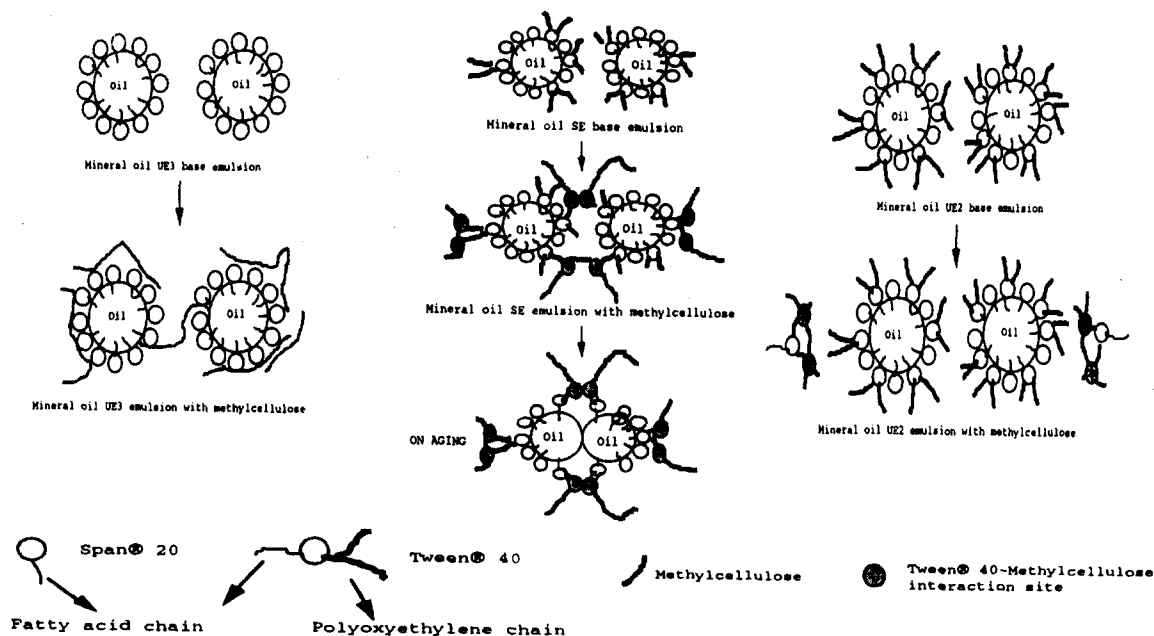

Fig. 7. Proposed stabilizing/destabilizing mechanism of mineral oil emulsions in the presence of Span® 20, Tween® 40 and methylcellulose.

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