

## Emulsion stability of cosmetic creams based on water-in-oil high internal phase emulsions

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### Abstract

The emulsion stability of cosmetic creams based on the water-in-oil (W/O) high internal phase emulsions (HIPEs) containing water, squalane oil and cetyl dimethicone copolyol was investigated with various compositional changes, such as electrolyte concentration, oil polarity and water phase volume fraction. The rheological consistency was mainly destroyed by the coalescence of the deformed water droplets. The slope change of complex modulus versus water phase volume fraction monitored in the linear viscoelastic region could be explained with the resistance to coalescence of the deformed interfacial film of water droplets in concentrated W/O emulsions: the greater the increase of complex modulus was, the more the coalescence occurred and the less consistent the emulsions were. Emulsion stability was dependent on the addition of electrolyte to the water phase. Increasing the electrolyte concentration increased the refractive index of the water phase, and thus decreased the refractive index difference between oil and water phases. This decreased the attractive force between water droplets, which resulted in reducing the coalescence of droplets and increasing the stability of emulsions. Increasing the oil polarity tended to increase emulsion consistency, but did not show clear difference in cream hardness among the emulsions.

**Keywords :** cosmetic cream, high internal phase emulsion, rheological consistency, electrolyte, oil polarity, water phase volume fraction

### 1. Introduction

High internal phase emulsions (HIPEs) are classed as emulsions with an internal phase volume above 74.05%. The existence of emulsions which contain a high internal phase volume ratio greater than 9 has long been known (Lissant and Mayhan, 1973). More recently, both oil-in-water (O/W) (Bergeron and Sebba, 1987) and water-in-oil (W/O) (Kunieda *et al.*, 1987; Kunieda *et al.*, 1989) systems with internal phase volume ratios of 99 have been prepared and studied. Such systems are biliquid foams with the continuous phase forming lamella between the distorted droplets of the internal phase. Because the droplet sizes are of the order of 1  $\mu\text{m}$  in diameter, their formation requires more surfactant than that for the preparation of typical emulsions, and the systems display gel-like properties. They have a number of actual and potential applications, some of which are mayonnaise in food, gels and creams in cosmetic products, petroleum gels as safety fuels, oil

recovery from oil sands, and agricultural sprays with pesticidal properties (Cameron and Sherrington, 1996). Particularly, one of the most important applications of HIPEs is their ability to be used as open microcellular foams by the polymerization of oil phase, the structure of which is quite different from the oriented, irregular and anisotropic structure of commercial blown and extruded foams (Barby and Haq, 1982). Open microcellular foams show highly porous characteristics with regular, spherical and isotropic structure (Stokes and Evans, 1997; Jeoung *et al.*, 2002; Choi *et al.*, 2003). A number of applications in this area include polymeric membranes, ion exchange resin, controlled release systems and inertial confinement fusion targets (Duke *et al.*, 1998; Wakeman *et al.*, 1998).

Understanding of the factors that govern the formation and stability of HIPEs is very rudimentary at present. There are, however, a number of important experimental observations that will undoubtedly be stepping-stones to enhanced understanding. From recent literatures, it is clear that the gel-like properties of W/O systems stem from the properties of the continuous oil phase. The W/O systems are formed, using nonionic surfactants, only in a temper-

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ature range above the HLB (hydrophile-lipophile balance) temperature, where the oil is expected to be a continuous phase. The penetration of oil molecules, specifically aromatic and short chain alkanes, into the surfactant layers is thought to be of importance in influencing the gel stability (Williams, 1988; Kunieda *et al.*, 1989). A further interesting observation is that electrolytes which cause a lowering of the cloud point of the surfactant in aqueous solution also confer stability on the W/O HIPE systems. Proper use of electrolytes appears to enhance the stability of highly concentrated W/O emulsions by increasing the resistance of the water droplets to coalescence (Aronson and Petko, 1993). Although all the above observations appear to be experimentally secure, there is currently little or no appreciation of their significance in terms of gel properties. Increasing the maximum amount of water phase against oil phase is also a matter of great concern. The ratio between the amount of water and oil phases to produce consistent emulsions depends upon the nature of emulsifiers, the polarity of oils, the concentration of electrolytes, and so on. Whether a certain ratio between two phases is accomplished or not is related to the operating conditions under which these emulsions are prepared, such as emulsifying method, power of mixing and mixing time.

In this study, the effects of electrolyte concentration and oil polarity on the viscoelastic properties of cosmetic creams were examined by varying water phase volume fraction. With increasing water phase volume fraction, changes in the complex modulus of emulsions monitored in the linear viscoelastic region were investigated. It was observed that the pattern of complex modulus change was closely related to the consistency of the W/O HIPEs. This relation could be explained with the resistance to coalescence of the deformed interfacial film of water droplets in the W/O HIPEs.

## 2. Experimental

### 2.1. Materials

Cetyl dimethicone copolyol (Abil EM 90) as an emulsifier for W/O creams and lotions was obtained from Goldschmidt Chemical and used without further treatment. Squalane, cyclomethicone (Silicone oil) and octyl dodecanol (Eutanol G) were obtained from Kishimoto, Dow Corning and Henkel, respectively. Glycerin was obtained from LG Chemical. Either magnesium sulfate ( $MgSO_4$ ) or sodium chloride (NaCl) is commonly used as an electrolyte to enhance the shelf life of cosmetic creams. In this study,  $MgSO_4$  was chosen and obtained from Wonjin Chemicals. Water was purified by reverse osmosis followed by passage through a Milli-RO 12 plus system. Conductivity of deionized (D. I.) water was determined to be 0.6 nS/m. Its surface tension was 71.9 mN/m at 25°C, in agreement with the value in literature (Timmermans, 1950).

**Table 1.** Ingredients and composition of emulsions used in this study [wt%]

Ingredient	Group E			Group P		
	E1-2	E2-2	E3-2	P1-2	P2-2	P3-2
Squalane	4.0	4.0	4.0	4.0	2.0	0.
Eutanol G	0.	0.	0.	0.	2.0	4.0
Silicone oil	13.0	13.0	13.0	13.0	13.0	13.0
Abil EM 90	2.0	2.0	2.0	2.0	2.0	2.0
D. I. water	to 100	to 100	to 100	to 100	to 100	to 100
Glycerin	5.0	5.0	5.0	5.0	5.0	5.0
$MgSO_4$	0.	0.3	0.5	0.	0.	0.

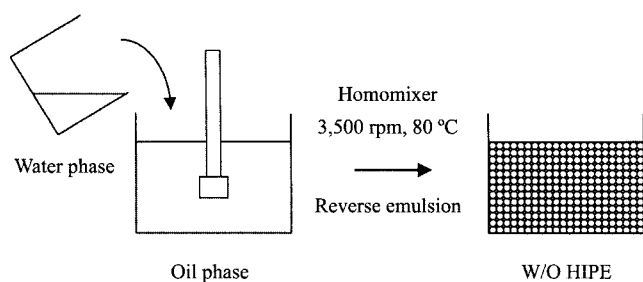
### 2.2. Preparation

The W/O HIPEs were prepared to investigate a relation between the rheological consistency of emulsions and the increasing pattern of complex modulus with increasing water phase volume fraction. The emulsion formulations are summarized in Table 1, in which their water phase volume ratio is maintained at 0.81. The concentration ranges of  $MgSO_4$  and Eutanol G were determined by considering emulsion appearances such as fineness and spreadability that was evaluated sensorially. In the two categories considered, the former group named E is to incorporate electrolyte into inner water phase, and the latter group named P is to vary the polarity of outer oil phase. In group E, the first number following E denotes the concentration of electrolyte, and in group P, the first number denotes the polarity of oil. The last number following hyphen stands for the water phase volume fraction, *i.e.*, the number 2 indicates the volume fraction of 0.81. In order to measure the pattern of complex modulus change with respect to the water phase volume fraction, two other samples having the water phase volume fractions of 0.78 and 0.85 were also prepared for both groups. Accordingly, the last number was given to differentiate the water phase volume fraction such as 1 for 0.78 and 3 for 0.85.

Both the oil and water phases were heated to 80°C for homogeneous mixing. While the oil phase was stirred, the water phase was slowly poured into the oil phase to produce the emulsion as uniform as possible. Emulsification proceeded simultaneously using a homomixer at 3,500 rpm for 10 min. A schematic diagram of simplified procedure for the preparation of W/O HIPE systems is shown in Fig. 1.

### 2.3. Characterization

The rapid assessment of the stiffness or rigidity of materials is very desirable objective. In this study, the cream hardness of the samples kept in 25°C chamber was measured using a Fudoh rheometer (Fudoh Kogyo, Japan) to check the rheological consistency of emulsions for 2 months. The measuring cup was filled with sample. Immediately after removal of excess sample, a stainless steel cyl-



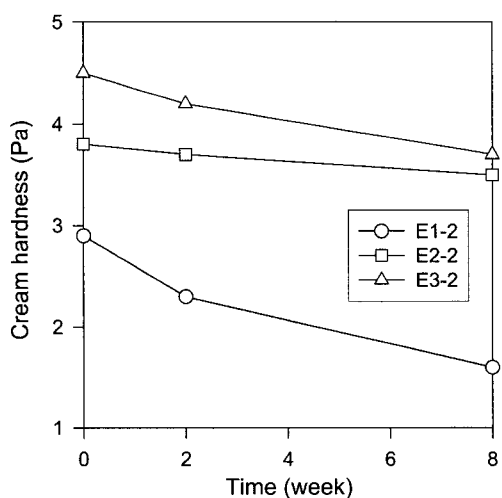
**Fig. 1.** Schematic diagram for the preparation of W/O HIPE systems.

inder was used to push down on the sample. The maximum load was recorded as cream hardness. Refractive index was measured using an Abbe refractometer (Atago, Japan).

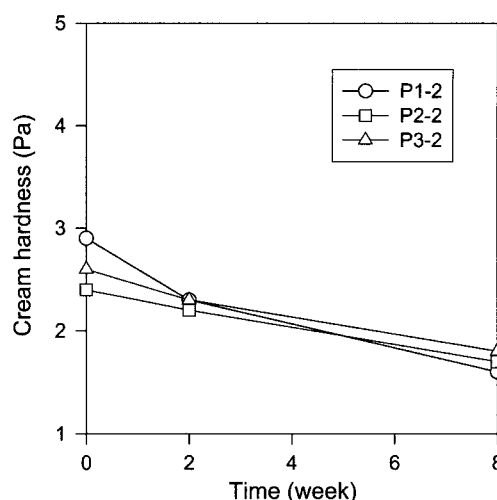
To measure the complex modulus,  $G^*$ , and the loss angle,  $\delta$ , of emulsions, small-amplitude oscillatory-shear test was carried out on all samples using RheoStress 50 (Haake, Germany). The cone and plate module with 35 mm in diameter and cone angle of  $1^\circ$  was used. Measuring temperature was maintained at  $25.0 \pm 0.2^\circ\text{C}$  by a Peltier Plate temperature controller (Model TC80). Stress sweep test was carried out and complex modulus in the linear viscoelastic region was monitored on each sample.

### 3. Results and discussion

The results for rheological consistency depending on time and electrolyte concentration are shown in Fig. 2. The addition of  $\text{MgSO}_4$  to the water phase of HIPEs had a substantial effect on cream hardness. However, care should be taken to draw a general conclusion because it is reported that the nature of the electrolyte used was found to be important (Kunieda *et al.*, 1989). In this experiment con-



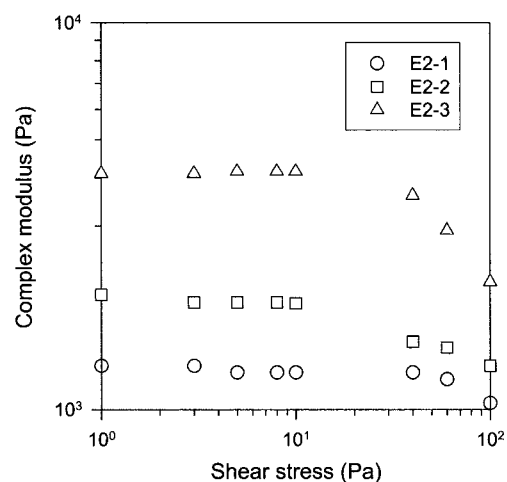
**Fig. 2.** Cream hardness change of group E with time and electrolyte concentration at a given water phase volume fraction.



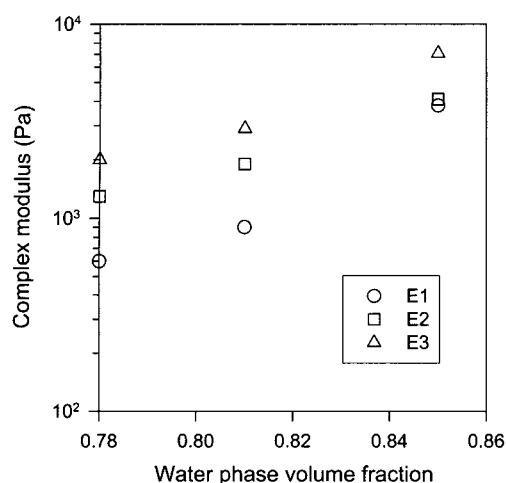
**Fig. 3.** Cream hardness change of group P with time and oil polarity at a given water phase volume fraction.

ducted at the water phase volume fraction of 0.81, the sample with 0.3 wt% of  $\text{MgSO}_4$  (sample E2-2) was the most consistent with time, whereas the sample without electrolyte (sample E1-2) was the least among three samples.

In analogous manners, the results for rheological consistency depending on time and oil polarity are shown in Fig. 3. The use of Eutanol *G* as a polar oil instead of squalane as a nonpolar oil had a slight effect on cream hardness. The samples P2-2 and P3-2 showed similar behavior with time and the sample P1-2 showed the largest decrease in cream hardness, *i.e.*, the least consistent among three samples. Since the oil polarity affects the stability of emulsions, proper control of oil polarity is very important for the preparation of consistent emulsions but it is difficult to quantify an optimal portion of polar oil at the present stage.



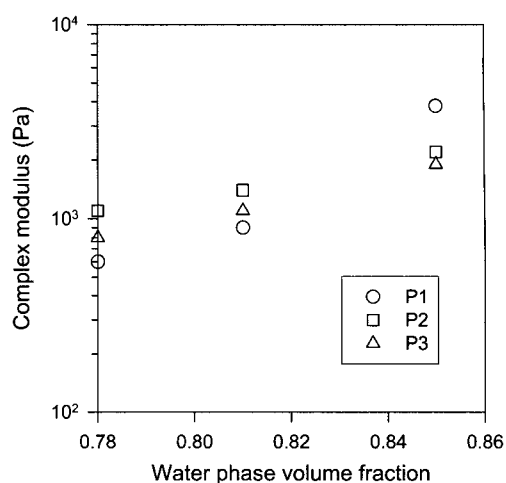
**Fig. 4.** Complex modulus change of group E with shear stress and water phase volume fraction at a given electrolyte concentration.



**Fig. 5.** Complex modulus change of group E with water phase volume fraction and electrolyte concentration.

The rheological responses for the stress sweep of the samples of group E with 0.3 wt% of  $\text{MgSO}_4$  are shown in Fig. 4, where the water phase volume fraction varies from 0.78 to 0.85. The increase of complex modulus monitored in the linear viscoelastic region is clearly seen with increasing water phase volume fraction. The increasing pattern of complex modulus can be explained as follows. As the water phase volume fraction increases, the solvate shell is more reduced or the interfacial layer is more compressed. Interfacial layers should be very stable to ensure the emulsion stability of HIPEs against coalescence. If not so, interfacial layers would be broken down and consequently water droplets would be coalesced.

The increasing patterns of complex modulus depending on water phase volume fraction are shown in Fig. 5, where all the data were evaluated within the linear viscoelastic region. The results show that the sample series without  $\text{MgSO}_4$  (E1-series) is the steepest in slope, whereas the sample series with 0.3 wt%  $\text{MgSO}_4$  (E2-series) shows the lowest increase. From the results of rheological consistency of the W/O HIPEs as already shown in Fig. 2, it can be said that the coalescence between two droplets or more would be minimal when the interfacial layer was formed stably. It was shown in Fig. 2 that the sample E2-2 was the most consistent and the sample E1-2 was the least, where the consistency was evaluated by aging test at a given water phase volume fraction. On the other hand, the pattern of complex modulus increase versus water phase volume fraction shown in Fig. 5 is speculated to represent an ability of interfacial layers of the W/O HIPEs to resist to the coalescence of water droplets. Namely, the greater the increase of complex modulus was, the more the coalescence occurred and the less consistent the concentrated emulsions were. Using this idea that emulsion consistency is possibly evaluated by the slope change of complex modulus depending on water phase volume fraction, the rheological



**Fig. 6.** Complex modulus change of group P with water phase volume fraction and electrolyte concentration.

consistency of cosmetic creams evaluated by aging test over several months can be predicted on the spot.

The same methodology was applied to the samples with different oil polarity (group P). Complex modulus change with oil polarity and water phase volume fraction are shown in Fig. 6. While the sample series P1 shows abrupt and stiff increase in slope that is an indication of poor consistency, the sample series P2 and P3 show linear and mild increase in slope, indicative of good consistency. The results in Fig. 6 are well matched with those in Fig. 3, although the hardness changes are not so dramatic as those of group E in Fig. 2.

The presence of electrolytes in water phase modifies several stabilizing factors operating in the system. Firstly, electrolyte influences the Ostwald ripening or coalescence. Since the chemical potential of water is higher in small droplets, there will be an active water transport from smaller to larger water droplets. The driving force of this process depends on the interfacial tension,  $\gamma$ , between two phases and can be expressed at the following equation for the rate of Ostwald ripening (Cho, 1997),  $\omega$ :

$$\omega = \frac{dr_c^3}{dt} = \frac{8\gamma c^{eq} V_m D \psi(\phi)}{9RT} \quad (1)$$

where  $\gamma$  is the interfacial tension,  $V_m$  is the molar volume of the substance of dispersed phase,  $r_c$  is the critical radius of a droplet which at a given time is neither growing nor dissolving. In most cases, the radius may be approximated by the average radius of droplets. The quantity  $c^{eq}$  is the dimensionless solubility of the bulk-dispersed phase in medium.  $D$  is the diffusion coefficient of the dissolved oil in water phase.  $R$  and  $T$  are gas constant and temperature, respectively. The coefficient  $\psi(\phi)$  reflects the dependence of the Ostwald ripening rate on the volume fraction,  $\phi$ , of droplets. The interfacial tension between the oil and water phases in the system was about 0.5 mN/m or less. Since

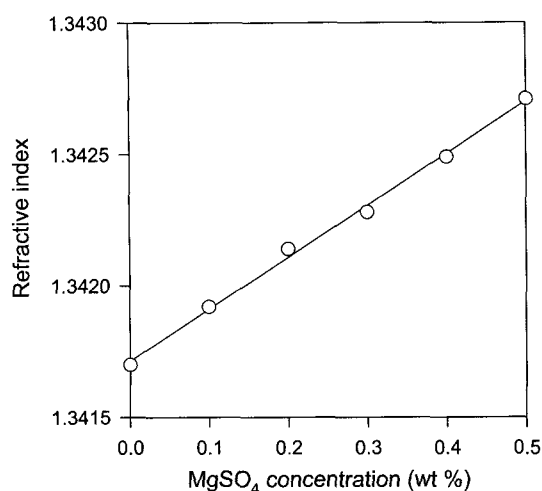


Fig. 7. Refractive index change of water phase with electrolyte concentration.

this tension is rather low and the pressure difference or the rate of Ostwald ripening between small and large droplets is very small, the driving force for Ostwald ripening is negligible. Thus the dominant factor for the change of droplet size is rather coalescence than Ostwald ripening.

The second factor influencing the emulsion stability of W/O HIPEs with electrolytes is that electrolyte lowers the attractive force between the water droplets across the thin organic film. The attractive force,  $W_a$ , between two aqueous droplets in the organic continuous phase is expressed as (Israelachvili, 1992).

$$W_a = a \left[ \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2} \right]^2 + b \frac{(n_1^2 - n_2^2)^2}{(n_1^2 + n_2^2)^{3/2}} \quad (2)$$

where  $n_i$  and  $\epsilon_i$  are respectively the refractive index and the dielectric constant of phase  $i$ , and  $a$  and  $b$  are constants. From Eq. (2), it is seen that the attractive force is at minimum when the refractive indices of the two phases are matched. The refractive index of the organic phase is 1.36, while it is 1.34 for that of the aqueous counterpart. Fig. 7 shows the refractive index of the water phase with varying electrolyte concentration. When electrolyte is added, the refractive index of the water phase is increased. Adding electrolyte into water phase, thus, decreases the attractive force between water droplets so that the emulsion gets more stabilized. The rheological results show that the emulsions with electrolyte are much more stable than those without electrolyte, which goes well with Eq. (2). But the emulsion containing 0.5 wt% of  $\text{MgSO}_4$  is not so stable as the emulsion containing 0.3 wt% of  $\text{MgSO}_4$ , from which we know that the stabilization of emulsions by the addition of electrolyte cannot be completely explained by the second term alone on the right side of Eq. (2) and that the first term of right side should be considered to assess the effect of electrolyte on emulsion stability. Evaluation on the term relating to dielectric constants needs more studies.

## 4. Conclusions

On the basis of the rheological investigation, the following conclusions concerning the stability of W/O HIPEs could be drawn: Firstly, it is speculated that the increasing pattern of complex modulus versus water phase volume fraction represents an ability of interfacial layers of W/O HIPEs to resist to the coalescence of water droplets. From the pattern of complex modulus change with water phase volume fraction, the rheological consistency of emulsions can be predicted. Secondly, the choice of oils is important because this coincides with the requirements for the formation of the rigid liquid crystalline phase in emulsions, but the change in oil polarity of emulsions does not make distinct difference when our remarks are confined to the experimental results conducted in this study. Lastly, it is believed that proper addition of electrolyte into the water phase opposes the instability due to coalescence, and as a result, the rheological consistency of HIPEs increases.

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## List of symbols

$c^{eq}$	= dimensionless solubility [-]
$D$	= diffusion coefficient [ $\text{m}^2/\text{s}$ ]
$G^*$	= complex modulus [Pa]
$n_i$	= refractive index [-]
$R$	= gas constant [ $\text{J}/\text{mol}/\text{K}$ ]
$r_c$	= critical radius of droplet [m]
$T$	= temperature [K]
$V_m$	= molar volume [ $\text{m}^3/\text{mol}$ ]
$W_a$	= attractive force between droplets [N]
$\gamma$	= interfacial tension coefficient [N/m]
$\delta$	= loss angle [degree]
$\epsilon_i$	= dielectric constant [-]
$\phi$	= volume fraction [-]
$\psi(\phi)$	= coefficient reflecting the dependence of Ostwald ripening rate [-]
$\omega$	= rate of Ostwald ripening [ $\text{m}^3/\text{s}$ ]

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