

# Stability of High Internal Phase Emulsions

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## Abstract

We have studied the stability of W/O high internal phase emulsions(HIPE) containing water, cetyl dimethicone copolyol and oils varying magnesium sulfate in the range 0 to 0.5 wt % and oil polarities, respectively. The rheological consistency was mainly destroyed by the coalescence of the deformed water droplets. The greater the increase of complex modulus was, the less coalescence occurred and the more consistent the concentrated emulsions were. The increasing pattern of complex modulus versus volume fraction has been explained with the resistance to coalescence of the deformed interfacial film of water droplets in concentrated W/O emulsion. The stability is dependent on: (i) the choice of the oil is important, the requirements coincide with the requirements for the formation of the rigid liquid crystalline phases; and (ii) addition of salts the aqueous phase opposes the instability due to coalescence. Increasing the salt concentration increases the refractive index of the aqueous phase. It lowers the difference in the refractive index between the oil and aqueous phases. This decreases the attraction between the water domains, thus increasing the stability.

## Key Words

Emulsion, Stability, Consistency, Coalescence, Rheology

## 1. Introduction

The existence of emulsions, termed high internal phase emulsions (HIPE), which contain a high internal phase volume ratio (greater than 9:1) has long been known (see e.g. ref. 1). More recently both oil-in-water (2) and water-in-oil (3-5) systems with internal phase volume ratios of 99:1 have been prepared and studied. Such systems are biliquid foams with the continuous phase forming lamella between the distorted droplets of the internal phase. Their formation requires more surfactant than that for the preparation of normal emulsions,

the droplets sizes are of the order of 1  $\mu$  diameter or less, and the systems display gel-like properties. They have a number of actual and potential uses.

Understanding of the factors which govern the formation and stability of HIPE is only very rudimentary at present. There are however a number of important experimental observations which will undoubtedly be stepping stones to enhanced understanding. From recent literature it is clear that the gel-like properties of water-in-oil systems stem from the properties of the continuous oil phase. Systems are only formed, using nonionic surfactants, in a temperature range above the HLB temperature (4), i.e., where the oil is expected to be a w/o microemulsion. The penetration of oil molecules (particularly aromatic and short chain alkanes) into the surfactant layers is thought to be of importance in influencing the gel stability (5,6). A further interesting observation is that salts which cause a lowering of the cloud point of the surfactant in aqueous solution (e.g. Na<sub>2</sub>SO<sub>4</sub>) also confer stability on the w/o HIPE. Although all the above observation appear to be experimentally secure, there is currently little or no appreciation of their significance in terms of gel properties.

The ratio between the maximum amount and the amount of continuous phase depends upon the nature of emulsifiers, the polarity of oils, the concentration of electrolyte and etc. This maximum amount depends upon the conditions under which these emulsions are prepared, such as power of mixing or mixing time.

In this paper the effect of varying the aqueous phase volume fraction on viscoelastic measurements was examined. With increasing aqueous phase volume fraction, the complex modulus of the emulsion increased. The increasing pattern of complex modulus with increasing aqueous phase volume ratio was investigated rather than maximum amount of internal phase was. We also observed that the increasing pattern of complex modulus is closely related to the consistency of W/O HIPE. The relation could be explained with the resistance to coalescence of the deformed interfacial film of water droplets in W/O HIPE.

## **2. Experimental**

### **2.1 Materials**

Cetyl dimethicone copolyol (Abil EM 90) was commercial grade obtained from Goldschmidt chemical company and used without purification. Cyclomethicone (Silicone oil), squalane and octyl dodecanol (Eutanol G) were obtained from Dow Corning (USA), Kishimoto (Japan) and Henkel (Germany), respectively. Glycerin was obtained from LG

chemicals(Korea) and magnesium sulfate( $\text{MgSO}_4$ ) was from Wonjin chemicals(Korea). Water was purified by reverse osmosis followed by passage through a Milli-RO 12 plus system. conductivity of water was determined to be  $0.6 \text{ nS m}^{-1}$ . Its surface tension was  $71.9 \text{ mN m}^{-1}$  at  $25^\circ\text{C}$ , in agreement with the best literature value(7).

## 2.2 Procedures

The W/O HIPE were prepared to investigate the relation between rheological consistency of emulsions and the increasing pattern of complex modulus with increasing internal phase volume. We considered two categories. The former group is to incorporate electrolyte into emulsions. The latter Group is to vary the polarity of outer phase, oils. The formulations are shown in Table 1.

The rigidity of above samples kept in  $25^\circ\text{C}$  chamber was measured using Fudoh rheometer to check the rheological consistency of emulsions for 2 months. The size change of deformed water droplets was examined using polarized microscope. In order to measure the increasing pattern of complex modulus with increasing internal phase volume, we made emulsions having different internal volume ratio for each sample. In sample E, the former number denotes salt concentration and in sample P, the former number denotes oil polarities. For example, in case of sample E1-2, we made two other samples having internal volume ratio 0.78 and 0.85 respectively. Then the sample having internal volume ratio 0.78 was named E1-1 and the sample with 0.85 was E1-3. The last number following hyphen was denoted to indicate internal volume ratio such as -1 for 0.78, -2 for 0.81 and -3 for 0.85 respectively.

Oscillation test was carried out on all samples to measure complex modulus and loss angle( $\delta$ ) using RheoStress RS 50 from HAAKE. Temperature is controlled  $25.0 \pm 0.2^\circ\text{C}$  by Peltier Plate Temperature Controller base(Model TC80). We used 35mm cone with angle  $1^\circ$ . From these results, the increase pattern of complex modulus versus internal volume ratio was checked.

## 3. Results and Discussion

### 3.1 For 1st Group - incorporation of $\text{MgSO}_4$

For group named 'E', the results for rheological consistency show that sample with 0.3 wt %  $\text{MgSO}_4$ (sample E2-2) is the most consistent with time among three samples (see Table 1 and Figure 1). The results for the increasing pattern of complex modulus show that sample without  $\text{MgSO}_4$  is the steepest in slope. The sample with 0.3 wt %  $\text{MgSO}_4$  shows the lowest

increase (see Table 2 and Figure 2).

### 3.2 For 2nd Group - different oil polarities

For group named 'P', the results for rheological consistency show that sample P2-2 and sample P3-2 show similar consistency with time and sample P1-2 shows the largest decrease in rigidity among three samples. The results for the increasing pattern of complex modulus show that sample P2-series and sample P3-series show similar increasing pattern of complex modulus and sample P1-series shows the largest increase (see Table 2 and Figure 3).

The results for the increasing pattern of complex modulus can be explained as follows. As the aqueous phase volume increases, the solvate shell is more reduced or interfacial layers are more compressed. The rheological response can be seen as increase of the complex modulus (Figure 4). To guarantee a high emulsion stability against coalescence, interfacial layer should be very stable. If not so, interfacial layer would be broken down and consequently water droplets would be coalesced. Thus, it can be said from the results of rheological consistency that in case of W/O HIPEs the less coalescence occurred, the more stable the interfacial layer is. The results show that the greater the increase of complex modulus was, the less coalescence occurred and the more consistent the concentrated emulsions were. Thus, the increasing pattern of complex modulus versus internal phase volume ratio could represent an ability of interfacial layers of W/O HIPEs to resist to a coalescence of water droplets.

### 3.3 Stability of HIPEs

The presence of salts in the aqueous phase modifies several stabilizing factors operating in the system. Firstly, salt influences the Ostwald ripening or coalescence. 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 the phases and can be expressed at the following equation for the rate of Ostwald ripening(8),  $\omega$ :

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

where  $\gamma$  is the interfacial tension,  $V_m$  is the molar volume of the substance of the dispersed phase ( $\text{m}^3 \text{mol}^{-1}$ )  $a$  is the radius of a droplet which at a given time is neither growing or dissolving. In most cases the radius may be approximated by the average radius. The

quantity  $c^{\infty}$  is the dimensionless solubility of the bulk dispersed phase in the medium, ( $m^3m^{-3}$ ) reduced to the density of the solute and  $D$  is the diffusion coefficient of the dissolved oil in the aqueous phase ( $m^2s^{-1}$ ).  $R$  is the universal gas constant and  $T$  is the absolute temperature. The coefficient  $\psi(\phi)$  reflects the dependence of the Ostwald ripening rate on the volume fraction ( $\phi$ ) of the droplets.

The interfacial tension between the oil and aqueous phases in the system was in order of  $0.5 \text{ mNm}^{-1}$  or less. This tension is rather low and the pressure difference, or rate of Ostwald ripening between small and larger droplets is very small and thus the driving force for the Ostwald ripening is negligible. Thus the reason for the change of droplets size was rather coalescence than Ostwald ripening.

The second factor influencing the stability of W/O HIPEs with salts is that salt lowers the attractive forces between the aqueous droplets across the thin organic film. The attractive force,  $W_a$ , between two aqueous droplets in the organic continuous phase is expressed as(9)

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

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 the equation [2] we see that attractive force is at minimum when the refractive index of the two phase is the same. The refractive index of the organic phase is 1.36, while it is 1.34 for aqueous phase. Figure 5 shows the refractive index of the aqueous phase with varying salt concentration. When salt is added the refractive index of the aqueous phase is increased. Adding salt into aqueous phase, thus, decreases attractive force between aqueous droplets so that the emulsion gets more stabilized. The rheological results show that the emulsion with electrolyte is much more stable than those without electrolyte, which goes well with the equation [2]. But the emulsion containing 0.5wt% of  $\text{MgSO}_4$  is not so stable as the emulsion containing 0.3wt% of  $\text{MgSO}_4$ , from which we know that stabilization of emulsion by addition of salt cannot be completely explained only by the equation [2] and that second term of right side of equation [2] should be considered to assess the effect of salt on emulsion.

On the basis of the present investigation we are able to draw two important general conclusions concerning the stability of HIPEs; (i) the choice of the oil is important, the requirements coincide with the requirements for the formation of the rigid liquid crystalline phases; and (ii) addition of salts into the aqueous phase opposes the instability due to coalescence but the effect of salt on the stability of HIPEs needs more studies relating to

dielectric constants.

## References

1. K.J. Lissant and K.G. Mayhan, *J. Colloid Interface Sci.*, 42, 201 (1973).
2. V. Bergeron and F. Sebba, *Langmuir*, 3, 857 (1987).
3. H. Kunieda, C. Solans, N. Shida and J.L. Parra, *Colloids and Surfaces*, 24, 225 (1987).
4. C. Solans, N. Azemar and J.L. Parra, *Prog. Colloid Polym. Sci.*, 76, 224 (1988).
5. H. Kunieda, N. Yano and C. Solans, *Colloids and Surfaces*, 36, 313 (1989).
6. J.M. Williams, *Langmuir*, 4, 44 (1988).
7. J. Timmermans, *Physicochemical Constants of Pure Organic Compounds*, Elsevier, Ed., New York, 1950.
8. W-G. Cho, PhD Thesis, University of Hull, UK, 1997.
9. J. Israelachvili, *Intermolecular and Surface Forces*, 2<sup>nd</sup> Ed., Academic Press, London, 1992.

Table 1. Formulations for measuring rigidity(unit: wt %).

Name of sample	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	-
Eutanol G	-	-	-	-	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
Glycerine	5.0	5.0	5.0	5.0	5.0	5.0
MgSO4	-	0.3	0.5	-	-	-

Table 2. Rigidity change with time(Rigidity in dyne/cm<sup>2</sup>).

Sample name	Group E			Group P		
	E1-2	E2-2	E3-2	P1-2	P2-2	P3-2
initial	29	38	45	29	24	26
after 2 weeks	23	37	42	23	22	23
after 2 months	16	35	37	16	17	18

Table 3. Increase of complex modulus with increasing aqueous phase volume ratio (complex modulus in Pa).

Sample name (aqueous phase volume ratio)	Group E			Group P		
	E1	E2	E3	P1	P2	P3
-1 (85%)	3800	4100	7100	3800	2200	1900
-2 (81%)	900	1900	2900	900	1400	1100
-3 (78%)	600	1300	2000	600	1100	800

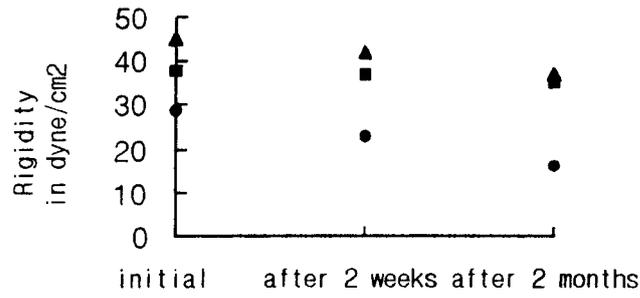


Fig.1 Rigidity Change of Group E depending on aging (Filled triangle stands for E3-2, filled rectangular for E2-2, and filled circle for E1-2)

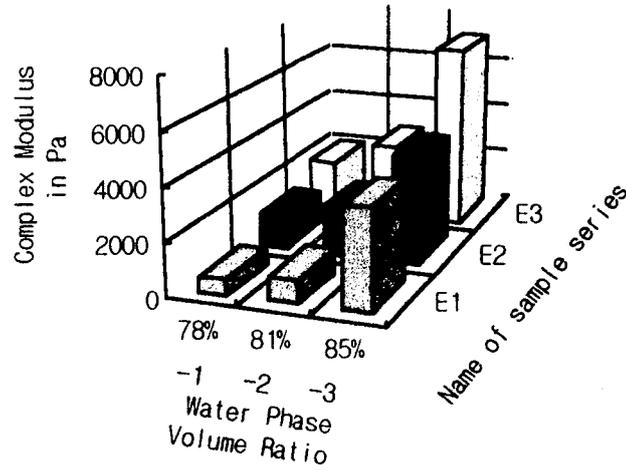


Fig.2 Complex Modulus Change of Group E versus Water Phase Volume Ratio

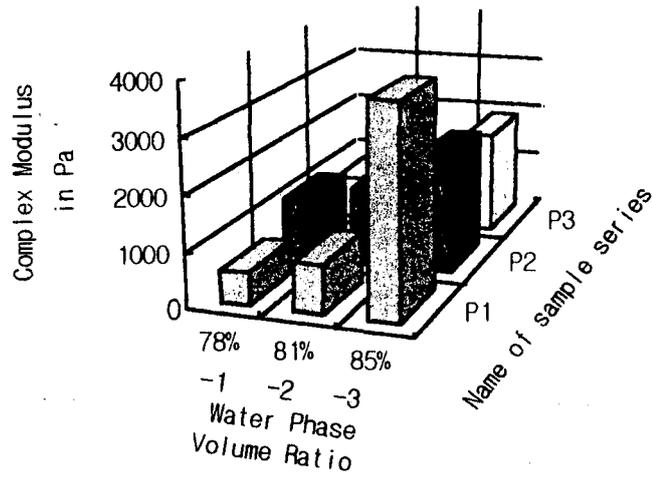


Fig.3 Complex Modulus Change of Group P versus Water Phase Volume Ratio

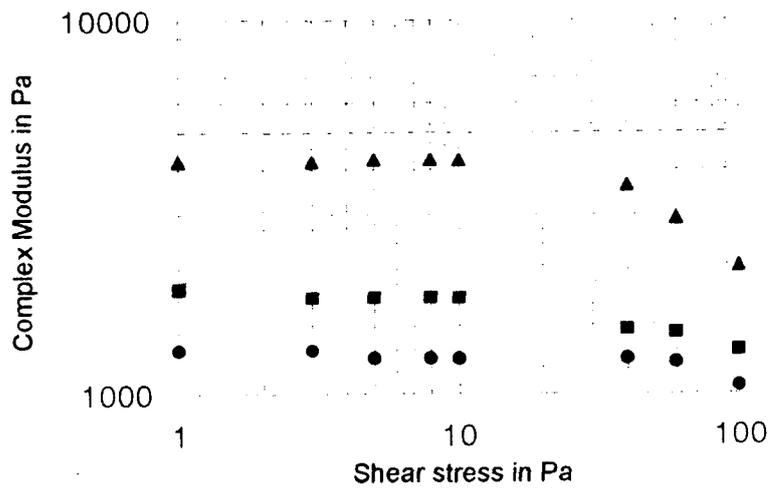


Fig.4 Rheogram of Stress Sweep test for E2 Series (Filled triangle stands for E2-1, filled rectangular for E2-2, and filled triangle for E2-3)

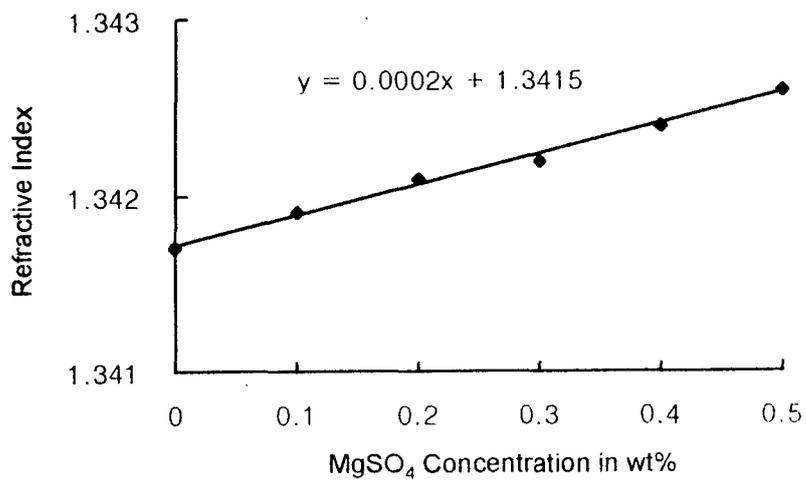


Fig.5 Refractive indices of aqueous phases varying salt concentration