# Cosmetic Emulsions

# 1. Emulsions

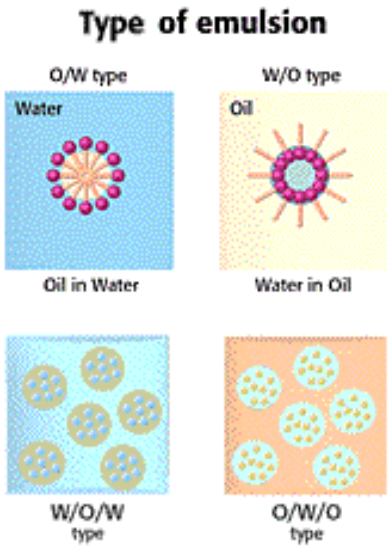
- Mixture of immiscible liquids, one liquid (dispersed phase) being dispersed in the other (continuous phase)

## (1) Types of emulsion

① Oil in water emulsion (O/W): non sticky, light, & moisturizing feeling
- oil: dispersed phase (oil component: 1-25%)
- water: continuous phase

② Water in oil (W/O): oily feeling, for products (*e.g.*) cleansing creams, cream foundations
- water; dispersed phase
- oil: continuous phase

③ Multiple emulsion



## (2) Building formula

- Most commercial creams and lotions have three building blocks:
  - Water phase
  - Oil phase
  - Miscellaneous phase

- an example of water phase:

| | |
|---|---|
| water | QS |
| humectant | 2-7% |
| preservative | 0.05-1.0% |
| thickener | 0.1-2% |
| "actives" | ? |

QS: 'as much as is sufficient"

- an example of oil phase:

| | |
|---|---|
| emollients | 5-10% |
| "actives" | drug level |
| antioxidant | 0.05-0.2% |
| emulsifier (primary) | 1-2% |
| emulsifier (secondary) | 1-2% |
| wax | 0.5-2% |
| silicones | 0.5-5% |

- an example of miscellaneous phase: fragrance 0.25%

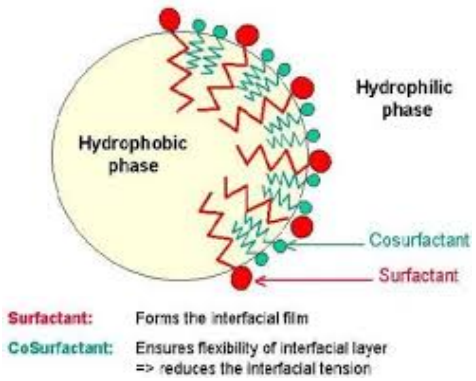
## (3) Emulsification: The process by which emulsions are prepared

○ **Emulsion** : ┌ thermodynamically unstable system
└ but can be kinetically stable over time period → requires 'stabilizer'

- Stabilizers:
  - Emulsifiers: surfactants adsorbing to the surfaces of interfaces of the system
  - Texture modifiers: slow down the movement of droplets
    ┌ increase viscosity of continuous phase (thickening agent)
    └ forms a gel network with the continuous phase (gelling agent)

○ **Types of emulsion vs. size**

- macroemulsion : particle size > 400 nm (appearance: white opaque)
  - thermodynamically unstable but kinetically stable
  - prepared by high intensity mixing & stirring
- nanoemulsion? (miniemulsion) : 100-400 nm (blue white, semiopaque)
- microemulsion: < 100 nm (translucent ~transparent)
  - thermodynamically stable
  - requires cosurfactants: *e.g.*, short chain alcohols, glycols
    to further reduce O/W interfacial tension
    → to enable a spontaneous formation of a microemulsion



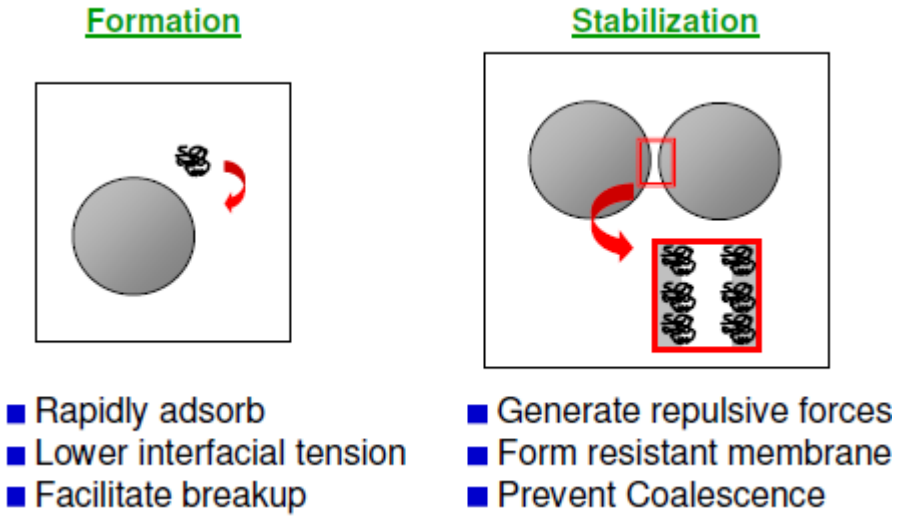
## (4) Role of emulsifiers

① Emulsion formation:

- by rapidly adsorbed to surfaces → lower interfacial tension → facilitate breakup

② Stabilization:

- by generating repulsive forces → form resistant membrane → prevent coalescence



# 2. Formulating Emulsions: HLB calculation

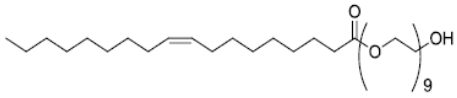
## 1) HLB system : Hydrophilic-lipophilic balance value

- used most in the rational selection of combination of nonionic emulsifiers
- stable o/w emulsion can be prepared by utilizing HLB method
- determined by the chemical composition and degree of ionization or hydration of the emulsifier molecule

○ **Griffn's method for calculating HLB**: to provide guidance for formulating with nonionic surfactants

- HLB = 20 x ($M_h$/M)
  - $M_h$ : molecular weight of hydrophilic groups
  - M: molecular weight of the whole molecule

(*e.g.*) PEG-monooleate




- $M_h$ $(OCH_2CH_2)_9$ = 396
- M = 671

∴ HLB = 20 x (396/671) = 11.8

# 2) HLB calculation

① Calculate the required HLB of oil phase → ② Calculate emulsifier ratio & amounts

## (1) Required HLB of oil phase

| Oil Class | Required HLB |
|---|---|
| Vegetable oils | ~6 |
| Silicone oils | 8-12 |
| Petroleum oils | ~10 |
| Typical esters | ~12 |
| Fatty acids; Fatty alcohols | 14-15 |

### ○ Required HLB Values of some ingredients

| | w/o | o/w |
|---|---|---|
| **Ingredient** | **emulsion** | |
| Acid, Lauric | -- | 15-16 |
| Acid, Oleic | -- | 17 |
| Acid, Stearic | 6 | 15 |
| Alcohol, Cetyl | -- | 15 |
| Alcohol, Lauryl | -- | 14 |
| Alcohol, Stearyl | -- | 14 |
| Lanolin, Anhydrous | 8 | 10 |
| Oil, Castor | 6 | 14 |
| Oil, Cottonseed | 5 | 10 |
| Oil, Mineral | 5 | 12 |
| Oil, Olive | 6 | 14 |
| Petrolatum | 5 | 12 |
| Wax, Beeswax | 4 | 12 |
| Wax, Paraffin | 4 | 11 |

## <Example calculation>

*Total oil content=76.2%

| | Component | Formula (%) | | HLB | Component in oil phase (%) | HLB contribution |
|---|---|---|---|---|---|---|
| oils | Naphthenic oil | 46.2 | | 8.5 | 60.63 (=46.2/76.2* x 100) | 5.154 (=8.5 x 0.6063) |
| | Fatty acid polyol ester | 20.0 | | 3.5 | 26.25 (=20.02/76.2* x 100) | 0.919 (=3.5 x 0.2625) |
| | Aminoalcohol 1* (3-amino-4-octaol) | 4.0 | | 6.3 | 5.25(=4.0/76.2* x 100) | 0.331 (=6.3 x 0.0525) |
| | Fatty acid | 6.0 | | 10.2 | 7.87(=6.0/76.2* x 100 | 0.803 (=10.2 x 0.0787) |
| surfactants | Sodium sulfonate surfactant | *x* ? | 20 | 7.0 | | |
| | monooleic acid ester | *y* ? | | 11.8 | | |
| | Aminoalxohol 2* (2-amino-2-methyl-1-prpaol) | 0.3 | | | | |
| | Glycol ether | 1.2 | | | | |
| | Water | 0.5 | | | | |
| | 1,2-Benzisothiazolin-3-0ne | 1.8 | | | | |
| | **Total** | **100** | | | | **7.21** |

## (2) Emulsifier calculation

- Recommended to use a blend of at least two emulsifiers
  - blend of a low HLB (primary) and a high HLB (secondary) surfactant

- Calculation

  $H * \%H + L * \%L = X * 100$ (X: required HLB, H: high HLB, L: low HLB)

  $H * \%H + L * (100-\%H) = X * 100$

  $$\%H = \frac{(X-L)}{(H-L)} * 100 \qquad \%L = 100 - \%H$$

  (*e.g.*) X = 7.2, H = 11.80, L = 7.0 → %H = 4.29, %L = 95.71

  ∴ x = 20% x 0.0429 = 0.86%

  y = 20% x 0.9571 = 19.14%

- Emulsion stability can be improved by adding a third emulsifier

(*e.g.*) ┌ Low HLB: 1:1 mixture of ┌ Sodium sulfonate surfactant (HLB: 7)
└ EO/PO block copolymer dioleate (HLB: 5)
└ High HLB: mono oleic acid ester (HLB: 11.8)

*Ref: www.ANGUS.com*

| Component | HLB | 1 | 2 | 3 |
|---|---|---|---|---|
| Naphthenic Oil | 8.5 | 46.2 | 46.2 | 46.2 |
| Fatty Acid Polyol Ester | 3.5 | 20.0 | 20.0 | 20.0 |
| Fatty Acid | 10.2 | 6.0 | 6.0 | 6.0 |
| Aminoalcohol 1* | 6.3 | 4.0 | 4.0 | 4.0 |
| Aminoalcohol 2* | | 0.3 | 0.3 | 0.3 |
| Natural Sodium Sulfonate | 7 | 7.92 | 8.37 | 8.02 |
| EO/PO Copolymer Dioleate | 5 | 7.92 | 8.37 | 8.03 |
| Mono Oleic Acid Ester | 11.8 | 4.16 | | |
| Alkyl Ether Carboxylic Acid | 13.4 | | 3.26 | |
| Secondary Alcohol Ethoxylates | 12.1 | | | 3.95 |
| Glycol Ether | | 1.2 | 1.2 | 1.2 |
| Water | | 0.5 | 0.5 | 0.5 |
| 1, 2-Benzisothiazolin-3-one | | 1.8 | 1.8 | 1.8 |
| Total | | 100 | 100 | 100 |
| pH Diluted Fluid | | 9.7 | 9.1 | 9.3 |
| Emulsion 24 hr | | Very good | Very good | Very good |
| Required HLB | | 7.21 | 7.21 | 7.21 |

- Choice of right low HBL emulsifier helps improve the emulsion stability

## ○ HLB Values of some surfactants (for nonionic surfactants)

| Surfactants | HLB |
|---|---|
| Sorbitan trioleate (Span® 85) | 1.8 |
| Sorbitan tristearate (Span® 65) | 2.1 |
| Sorbitan sesquioleate (Arlacel 83) | 3.7 |
| Glyceryl monostearate, N.F. | 3.8 |
| Sorbitan monooleate, N.F., (Span® 80) | 4.3 |
| Sorbitan monostearate, N.F., (Span® 60) | 4.7 |
| Sorbitan monopalmitate, N.F., (Span® 40) | 6.7 |
| Sorbitan monolaurate, N.F., (Span® 20) | 8.6 |
| Polyoxyethylene sorbitan tristearate (Tween® 65) | 10.5 |
| Polyoxyethylene sorbitan trioleate (Tween® 85) | 11.0 |
| Polyethylene glycol 400 monostearate | 11.6 |
| Polysorbate 60, N.F., (Tween® 60) | 14.9 |
| Polyoxyethylene monostearate (Myrj 49) | 15.0 |
| Polysorbate 80, N.F., (Tween® 80) | 15.0 |
| Polysorbate 40, N.F., (Tween® 40) | 15.6 |
| Polysorbate 20, N.F., (Tween® 20) | 16.7 |

NF: 'National Formulary'
NF Grade

## ○ HLB Values and types of emulsion formed

| Range of HLB value | Solubility in water | Emulsion type |
|---|---|---|
| 1–4 | Insoluble | Water-in-oil |
| 4–7 | Poor unstable dispersion | Water-in-oil |
| 7–9 | Stable opaque dispersion | – |
| 10–13 | Hazy solution | Oil-in-water |
| 13 and higher | Clear solution | Oil-in-water |

## ○ HLB value function for surfactants

| | |
|---|---|
| 1 - 3 | compatibilizing dissimilar oils, anti-foaming agent |
| 3 - 6 | water-in-oil emulsifier |
| 7 - 9 | wetting agent, wetting powders into oils |
| 7 - 10 | self emulsifying oils |
| 8 - 15 | oil-in-water emulsifier |
| 12 - 15 | formulating detergent |
| 15 - 18 | solubilizer, hydrotrope |

# 3) Emulsion properties

○ **Appearance and feel** :

- related with
  - viscosity
  - pour characteristics
  - gloss/pearlescence/opacity
  - smoothness & texture

○ **Particle size**: has effects on

① viscosity

② appearance (roughly):
- > 1 μm: milky white
- 0.1-1 blue-white
- < 0.1 semitransparent (opalescent)
- <0.05 transparent

③ stability : depends on
- type and quantity of emulsifier
- the amount of work applied
- order of adding ingredients

○ **pH**: skin pH 4-6

○ **Viscosity**: adding thickeners increase viscosity
- polymers
- NaCl: only for anionic emulsion (∵due to reduction of charge density → more favorable association)

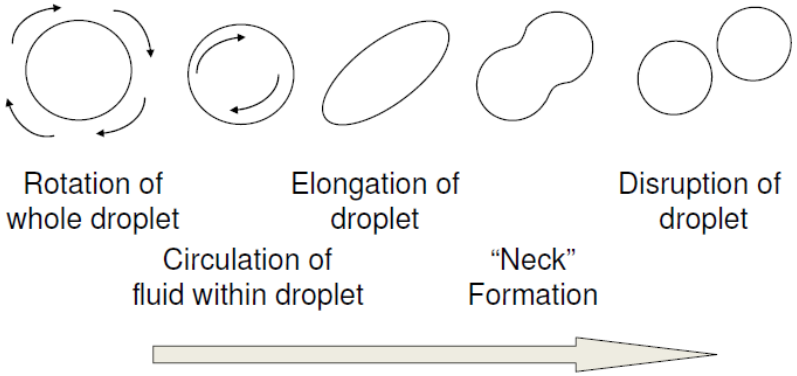
(*c.f.*, but nonionic emulsion gets thinner in the presence of NaCl)

## ○ Factors affecting emulsion properties, stability and type

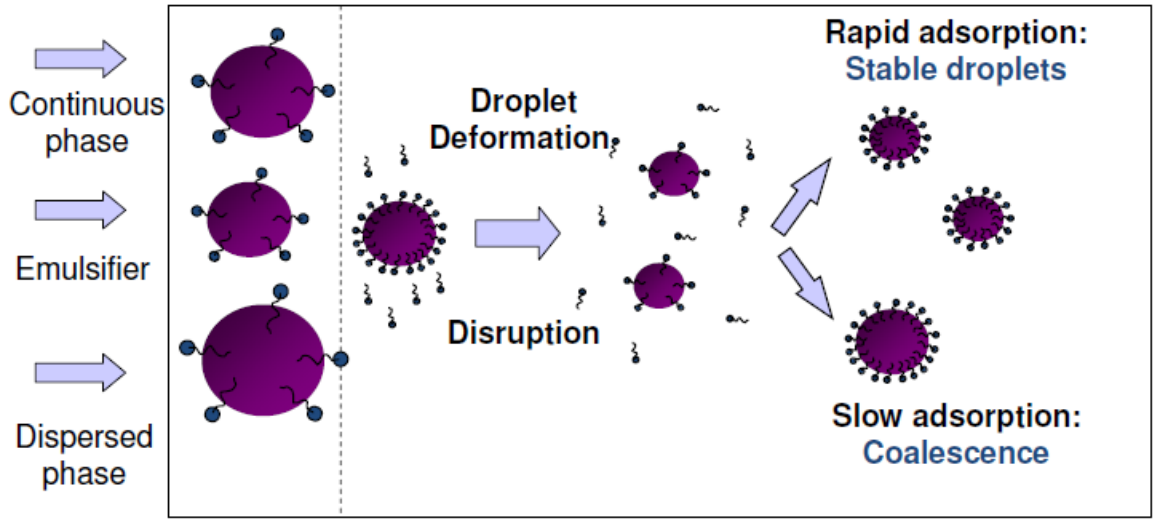
- physical and chemical properties of the oil and water phases
- phase-volume ratio of oil and water phases
- concentration of emulsifier
- pH:
  - anionic type emulsion pH>8; may separate at lower pH
  - nonionic emulsified products: pH 3-10
  - cationic emulsified product: pH 3-7
- order of ingredient addition
  - o/w emulsion: add oil phase to the water phase while heating
  - w/o emulsion: add water phase very slowly to the oil phase (which must contain emulsifier) with continuous stirring
    (More difficult to obtain stable W/O emulsion)
- temperature of emulsification
- type of equipment
- method and rate of cooling

# 3. Principle of Emulsion Formation

## (1) Dispersion process




## (2) Homogenization process



# 4. Emulsification Method

## ○ Emulsifier addition

- nascent soap method: alkali is added directly to oil
- emulsifier is added to oil phase: widely used in cosmetics
- emulsifier is added to aqueous phase
- phase-inversion emulsification: emulsifier is added to both phases
  phase inversion when cooled

## ○ Emulsification devices

- paddle mixer: emulsification without shearing the components
- disperser: not much strong shearing, useful for dispersing and dissolving polymers
- homomixer: - very effective for emulsifying cosmetics
  - by high speed mechanical and hydraulic shear forces
  - should be used for the initial stage of emulsification
  - long use destroys emulsion and cause destabilization and change in viscosity
- propeller mixer: for dissolving substances (not for emulsification)

(paddle mixer)


(disperser)

(homomixer)

(propeller mixer)


출석코드: cosmetics