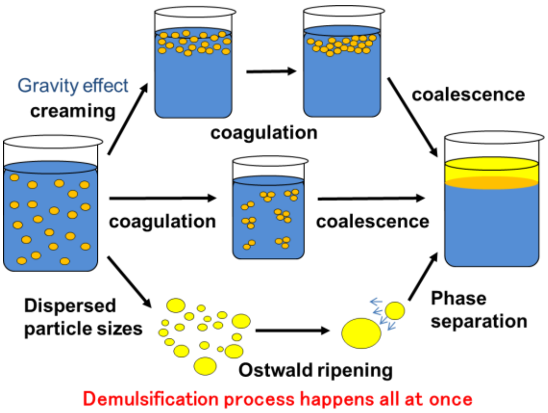
Accounts of Materials & Surface Research

Tips to improve emulsion stability from the view point of “Merely Emulsion, Nevertheless Emulsion”

Yuji Yamashita,[a] Kazutami Sakamoto[b]*
[a]Faculty of Pharmacy, Chiba Institute of Science, 15-8 Shiomi-cho, Choshi, Chiba, 288-0025, Japan.
[b]Faculty of Science and Technology, Tokyo Univ. of Science, 2641 Yamazaki, Noda, Chiba, 278-8510, Japan.
kazusaka@rs.noda.tus.ac.jp

Tips to improve emulsion stability from the view point of “Merely Emulsion, Nevertheless Emulsion” is explained. The “Merely” and “Nevertheless” aspects of emulsions and emulsification in actual formulation and development processes gives formulators hints to foresee problems and find solutions for the problems occurred. As a guide of tips, Utilization of Phase Diagrams, HLB, Bulk Physical Property Control, Controlling the Interfacial Phase are explained. These perspectives of “Merely” and “Nevertheless” will help when formulators face such problems and lead to developing better emulsion products.



Keyword: *Fundamental Nature of Emulsions, Utilizing Phase Diagrams, Utilizing HLB, EmulsificationTechnology, Interface Control*

Yuji Yamashita received his Ph.D. in natural science from Bayreuth University, Germany, in 2005, an M. S. and B. S. from Yokohama National University, Japan. After several years of research work on the thermotropic liquid crystals in industry laboratory at Chisso Petrochemical Co., he began to study dermatology, especially transdermal drug delivery system, as a post-doctor at St. Marianna University, Japan. Since October 2011, he has been engaged in teaching and research concerning the cosmetic science as an assistant professor at Chiba Institute of Science. The area of his expertise is the surfactant science such as phase behavior and self-assembly which is related to formulation technology.

Kazutami Sakamoto is a former professor of Graduate school of Pharmacy at Chiba Institute of Science. He is also an adjunct professor at Tokyo University of Science. He has received Ph. D. from Faculty of Science at Tohoku University in 1980. He has extensive R&D experiences in industry since 1971 to 2008 with Ajinomoto, Shiseido and Seiwa Kasei. He has elucidated pioneering research on the physicochemical properties of aminoacid based chiral surfactants, chiral mesoporous silica. Dr. Sakamoto received award from Japan Oils Chemists' Society in 2005. He was a Chairman of Division of Colloid and Surface Chemistry at The Chemical Society of Japan for 2007-2008. And he is a fellow of this society.

Tips to improve emulsion stability from the view point of "Merely Emulsion, Nevertheless Emulsion"

Yuji Yamashita,[a] Kazutami Sakamoto[b]*
[a]Faculty of Pharmacy, Chiba Institute of Science
[b]Faculty of Science and Technology, Tokyo Univ. of Science

1. Introduction

Emulsification is the process of mixing liquids that are otherwise immiscible to create a disperse system, and the disperse system created by this process are called emulsions. We often use dressing as an example of emulsion when teaching to novice students. To make dressing, we shake the container well to mix the oil and water, but the dressing separates back to its original state of oil and water once we stop shaking. In other words, energy such as mixing must be applied to disperse the immiscible liquids, and this leads to maximizing the interface area between the liquids, creating emulsion particles.

However, when this mixture is left in a static state, the particles start to join (coalesce) and interface area between these liquids become minimal, creating a two-phase oil-water system. This example of making dressing with immiscible water and oil can demonstrate the fundamental nature of emulsions. That is, emulsification is the process of making a disperse system from a mixture of liquids that would divide into different phases in equilibrium, such as water and oil phases, to create a dispersion and stability from this liquid in liquid disperse system to meet its desired functions.(Figure1) French dressing, salads with olive oil and balsamic vinegar, and dumpling sauce made with soy sauce, vinegar, and hot oil are all examples of how the delicate and instable mixture and separation of emulsions can create an enjoyable taste.[1] In other words, these are all food products that utilize the nonequilibrium and heterogeneous systems of emulsion.

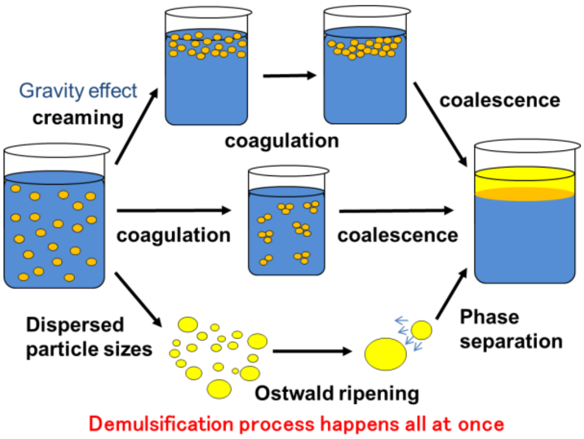


Figure 1. Demulusification Mechanism

Unlike these foods, butter (W/O) and milk (O/W), two example commonly used to explain emulsion, must have a stable disperse system with an optimal particle size and dispersion for creating its taste, and even have a specific rheological property that creates its texture. To create these characteristics, in common practice surfactants (emulsifiers) are used to reduce the interface energy during the emulsification process to facilitate the dispersion and viscosity modifiers are used to inhibit the cohesion and adhesion of the particles. In food products, many methods are tested to accordingly adjust the stability and delicacy of emulsions to create the desired taste and texture to enhance the foods and create enjoyable meals. However, in the field of cosmetics, typically a three-year shelf life is set as a quality standard.[2] To achieve this shelf life, cosmetic developers and researchers are faced with challenges to simplify the manufacturing processes and at the same time, create an emulsion that is stable but comfortable, properties that are often contrary. This is why basic research and application of emulsions in cosmetics are more fundamental compared to that of the food industry.

Emulsions can be made simply by mixing two liquids with force and stabilizing it by adding surfactants or emulsifiers (Merely Emulsion), but to make an emulsion that is comfortable, safe, and stable is not something that can be easily achieved (Nevertheless Emulsion). In this chapter, we will explore the fundamental nature of emulsions and real-world techniques of creating better products that overcome these challenges of emulsion.

2. Merely Emulsion

Emulsion systems are commonly found in nature, such as with bile acids that help the digestion and absorption of fats and oils, or in organic functions such as lipoproteins that carry fats in the body to create fundamental metabolism which carries substances within and also in and out of the organism's system. The system that controls and sustains this non-equilibrium state dynamically (homeostasis) is vital to stabilizing a natural emulsion with its required function. As mentioned above, there are many food products that utilize such stability and instability of emulsions. Most of these food emulsions are stable due to their complex system, and in many cases have solids or liquid crystals that stabilize the interface of the emulsion, helping them keep their required conditions such as shelf life. Due to these characteristics, such products can be manufactured using knowledge and craftsmanship earned from experience to make an emulsion that is stable enough with their desired functions.

Utilizing such craftsmanship and passing the skills to successors, it is not impossible to build a thoroughly managed manufacturing site and process and keep a constant quality in the emulsion manufacturing in cosmetics and medicine as well. In fact, there are many long-selling and trusted products such as hand creams that are manufactured with such strictly managed formulas and manufacturing processes, and each of these brands has their own unique formula and process to create their own characteristic emulsion product. However, this should not be perceived as "merely emulsion" or "easy to do." If this is taken for granted and the process management is not strict, factors such as the change of quality of the ingredients or up-scaling the production volume can often lead to problems with unknown causes.[2] To prevent such potential pitfalls and to resolve such issues at an early stage, we must understand that emulsions are fundamentally thermodynamic non-equilibrium systems, and must fully understand and utilize various emulsification theories. Only then can we manufacture practical emulsions with desired functions and create new products with new functions and characteristics. We must let go of the sense of "merely emulsion" or "easy to do" and look deeper into the complexity of emulsions and explore further to endeavor new horizons.

3. Nevertheless Emulsion

Dr. T.J. Lin has supported the cosmetics industry's emulsification process control and problem solving with his chemical engineering expertise in his long career, and Dr. Lin points out in his newest work that in recent years, problems are frequently caused from marketing-based product development and manufacturing.[2] For example, labeling all ingredients was introduced to inform proper information of the product to the consumers to prevent any problems caused by using the said product, but the original concept has been deviated to forcing the formulation developers to use ingredients based on concepts such as natural only ingredients. If these developers have little experience with such ingredients, their characteristics can cause an unexpected interaction and make the emulsion unstable, and if these developers are forced to omit ingredients that have been proven safe from years of experience such as paraben and EO emulsifiers for the sake of the product image, it can lead to manufacturing and quality control issues. In his foreword, Dr. Lin looks back at his experience as a novice engineer and jokingly states that these are "emulsion stability deteriorated" mistyped into "emotional stability deteriorated." In this sense, we may be facing a hard era for formula engineers; but their challenges continue, and we will look at some examples of "nevertheless emulsion" from several angles.

Dr. Lin introduces a new approach of emulsification process called Low Energy Emulsification, or LEE, to manage issues that can occur in up-scaling production or to handle the demands for today' s trend

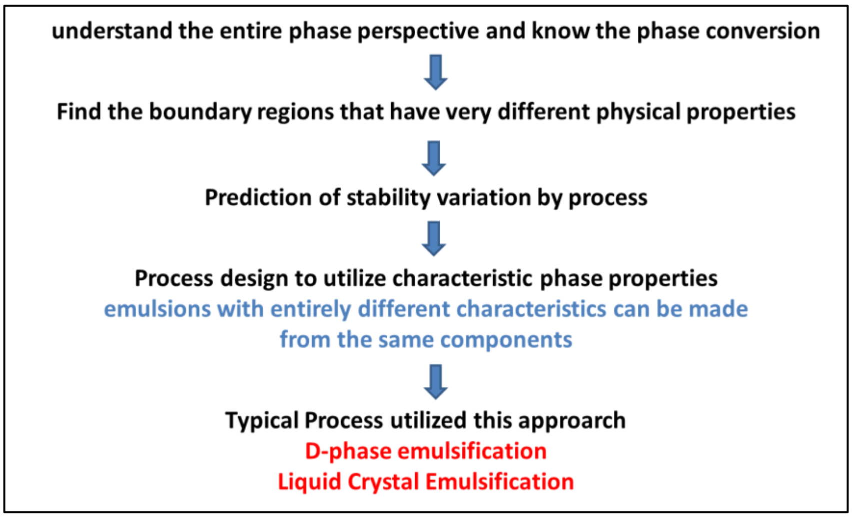


Figure 2. Utilization of Phase Diagram

Every surfactant has its own hydrophobic-lipophilic balance (HLB)
Property of each oil differs independently (required HLB)
HLB is a concept of collectively unifying and applying these properties

Phase Inversion Emulsification (PIT)
Systematic utilization of PIT to produce emulsion
with specific particle diameters and rheological properties and stability

Utilization of Microemulsion
One-phase liquid phase called (D phase) as microemulsion
at which components are mutually soluble in a
thermodynamically stable equilibrium

Figure 3. Utilization of HLB

towards low energy manufacturing. With this approach, Dr. Lin states that the key to understanding the importance of the processing factor is to fully realize that emulsions are thermodynamically unstable systems that will eventually separate into different phases. Formulation engineers and process designers must prove their skill with how they balance the desired stability with its comfort out of this fundamentally unstable system. Phase Inversion Emulsification, D Phase Emulsification, and Liquid Crystal Emulsification are successful methods established in Japan that achieve this balance. These emulsification methods share a technique of using triangle phase diagrams of the water phase, oil phase, and surfactant phase of the emulsion for their apex points.[3]

<Utilizing Phase Diagrams>

By understanding the entire perspective of the composing materials and knowing the phase conversion, this method can show the boundary regions that have very different physical properties from just a slight change in the content ratio. Understanding this visually makes it possible to design processes for emulsions with entirely different characteristics made from the same components. D phase emulsification and liquid crystal emulsification are typical methods that utilize this method. (Figure 2)

<Utilizing HLB>

Every surfactant has its own hydrophobic-lipophilic balance, or HLB, and the property of each oil differs independently (required HLB). HLB is a concept of collectively unifying and applying these properties, and phase inversion emulsification is a method of applying HLB with the thermal properties of phase inversion temperature (PIT) to produce an emulsion systematically with specific particle diameters and rheological properties and stability. Shinoda, Kunieda et al have established a theoretical foundation of these two methods through

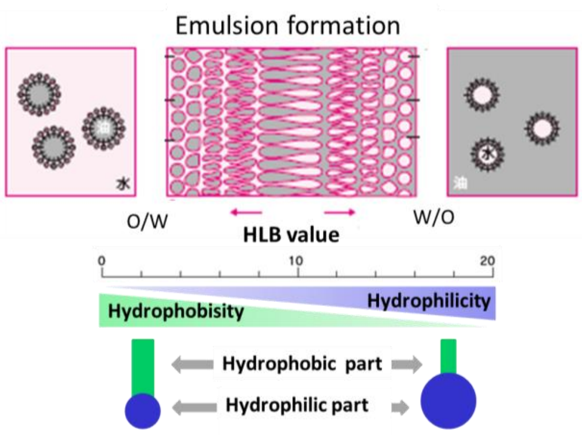


Figure 4. Structure and HLB

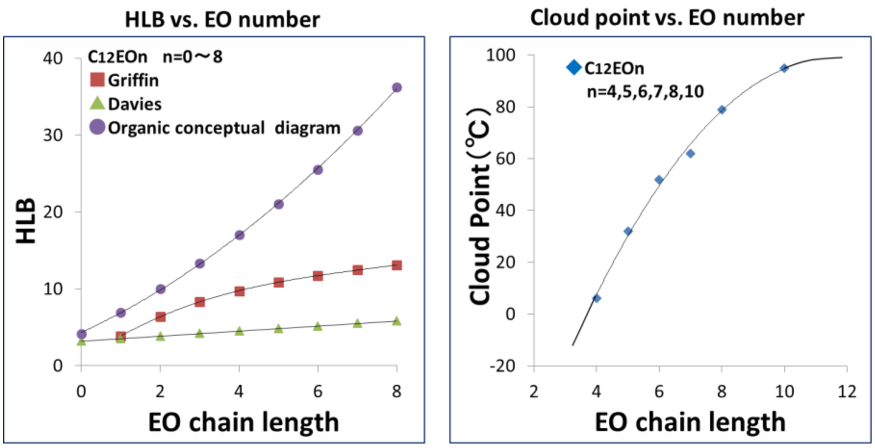
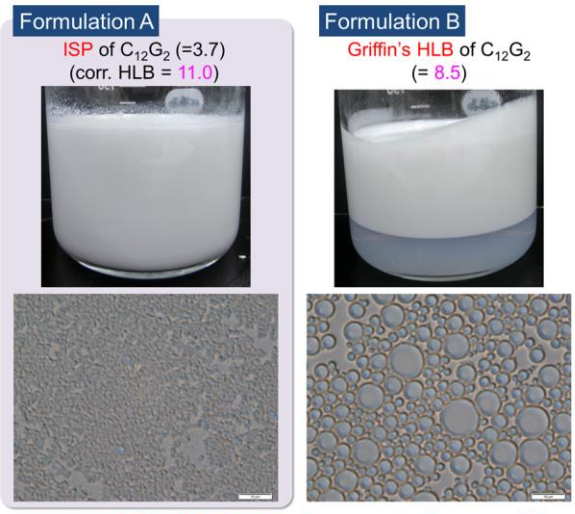


Figure 5. Drawbacks of HLB

their basic research by utilizing phase diagrams of EO surfactants and the solution states, and applications of their methods have greatly contributed to the industry. When the hydrophobic and lipophilic states of the surfactants are balanced, a high-density one-phase liquid phase called a D phase is created. This is customarily called microemulsions, but they are actually three components that are mutually soluble in a thermodynamically stable equilibrium. Microemulsions are applied to emulsions that are stable in ultrafine (nano-order distributed particles) levels, and also to new formulas such as those that are independently bicontinuous in the D phase with the water or oil phase.(Figure 3) These examples show how HLB are applied to emulsification processes, especially with EO emulsifiers. (Figure 4) However, HLB value are inconsistent by the method to calculate and would not correlate to the physicochemical properties such as cloud point. (Figure 5) Further to this, for polyglycerin emulsifiers, which are also non-ionic emulsifiers like EO emulsifiers, they show different thermal properties with similar HLB values thus HLB method are not always applicable to the different molecules . In such cases, organic conceptual diagrams are often tested to determine the HLB, but the value



Formulation A

Oil phase	
$C_{12}G_2$ (ISP=3.7) → corr. HLB 11.0	4g
Span (HLB 4.7)	
Liquid Paraffin (req. HLB 10)	40g
Aqueous phase	
Distilled Water	56g

Formulation B

Oil phase	
Tween (HLB 14.9)	4g
$C_{12}G_2$ (Griffin's HLB 8.5)	
Liquid Paraffin (req. HLB 10)	40g
Aqueous phase	
Distilled Water	56g

General emulsification tests using Tween (HLB 14.9) and Span (4.7) are carried out to evaluate $C_{12}G_2$ with unknown HLB.
ISP of $C_{12}G_2$ which takes as hydrophilic surfactant gives more stable emulsion than the Griffin's HLB corresponding to lipophilic surfactant.

With ISP for $C_{12}G_2$ gave better emulsion (A) than with HLB (B)

Figure 6. Drawbacks of HLB

of each substituent can only be set through experience and the rules for the position of the substituents are insufficient, so the experimental results can differ from what was predicted. We have recently developed new empirical parameter (ISP: integrated surfactant property) to characterize hydrophilic/hydrophobic properties of emulsifiers by utilizing TLC measurement.[4] We found ISP better correlate to the physicochemical properties both for EO type and glycerin type emulsifiers. With ISP we could easily prepare stable emulsion better than HLB. (Figure 6)

<Utilizing Bulk Physical Property Control>

The stability of emulsions as a product can be defined by characteristics such as the change in rheological property (i.e. change in the touch of the product can be perceived as quality deterioration) caused by interaction of the distributed particles, or two-phase liquid separation caused by the particles joining (aggregation and coalescence). In common practice, thickeners are used to prevent such changes. In recent years, emulsifications that are simple and do not require deep experience have been developed by using ampiphilic polymeric emulsifiers that can control the rheological properties in the bulk phase. The key to this method is to make a pre-mix of the polymeric emulsifier to make it more soluble, and every ingredient maker (supplier) have their own method of doing so. Controlling the bulk properties is a simple and reliable emulsification method, but further tasks remain on how to adjust the delicate touch and rheological property to make a characteristic uniqueness to the product.

<Utilization of Controlling the Interfacial Phase>

The instability of emulsions all comes down to the instability of the interface. Usually surfactants (emulsifiers) are used to decrease the interfacial tension and to stabilize the emulsion, but to maintain enough surface excess concentration, more surfactants are dissolved than that required for directly stabilizing the interface. If there are surfactants that exist (or distributed) only to the interfaces, we can expect an optimally efficient interface control. Recent topics such as three-phase emulsion and pickering emulsion are examples of this concept, but since there are few choices that offer enough flexibility for the various types of emulsion and oil phases that normal surfactants offer, there are still challenges remaining on how to apply this method to practical needs.

Recently, we have proposed an inclusive concept called Active Interfacial Modifier, or AIM.[5] AIMs are substances with substituents that have affinity for both of the immiscible phases, but do not dissolve in either of the phases. As a result, these AIMs are naturally distributed only to the interfaces, thus making the required amount minimal but can easily stabilize the interface (maximize the amount of interfacial area), or in other words, make an emulsion that is stable over a long period of time. The AIM concept occurred when making a three component mixture of hybrid polymer of silicone and peptide with water/silicone oil (Cyclopentasiloxane), and with simple method like Vortex mixers it could easily make a stable W/O emulsion in a wide variety of compositions.

4. Conclusion

In this chapter we have written our thoughts on the “Merely” and “Nevertheless” aspects of emulsions and emulsification as they crossed our mind, but in actual formulation and development processes, we must face various factors comprehensively, and at the same time specifically analyze the factors. I hope these perspectives of “Merely” and “Nevertheless” will help when you face such problems and lead to developing better emulsion products.

Reference

1) Masahiko Abe, Kazutami Sakamoto, Hiroshi Fukui, *Easy introduction to Surfactant*, Nikkan Kogyo Shinbun, **2010**, pp.10-11.

2) T. Joseph Lin, Hiromichi Sagitani, *Manufacturing Cosmetic Emulsions: Pragmatic Trouble Shooting and Energy Conservation*, Fragrance Journal, **2011**, 3 -11.

3) T. Horiuchi, *J. Soc. Cosmet. Chemists. Jpn.*, **2010**, *44(1)*, 2-22.; T. Suzuki, *J. Soc. Cosmet. Chemists. Jpn.*, **2010**, *44(2)*, 103-117.; T. Okamoto, *J. Soc. Cosmet. Chemists. Jpn.*, **2010**, *44(3)*, 199-207.; M. Hayase, *J. Soc. Cosmet. Chemists. Jpn.*, **2010**, *44(4)*, 269-277.

4) Y. Yamashita, K. Sakamoto, *The Bulletin of Chiba Institute of Science*, **2013**, *6*, 89-92.

5) K. Sakai, et al., *Langmuir*, **2010**, *26(8)*, 5349-5354.