Chapter 1

Introductory Chapter: The Perspective of Emulsion Systems

Selcan Karakuş

Additional information is available at the end of the chapter

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1. Introduction

Emulsions (0.1–100 mm) are metastable systems and commonly used in our daily life. They are extensively preferred on many industrial processes in the food, beverage, dye, detergent, drug, cosmetic, coating, technological areas, agricultural, and petroleum production due to their special rheological (yield stress, viscosity and storage or loss modulus) and antibacterial properties [1–3]. Generally, synthesis methods for emulsion systems are stirring, colloid mills, and high-pressure homogenizers [4, 5].

2. Emulsion: Types anproperties

Emulsions are thermodynamically unstable (coalescence, sedimentation/creaming, flocculation, Ostwald ripening, and phase inversion) and are provided with kinetic stability by surfactant molecules for weeks, months, or years. The average particle size and its distribution are crucial factors for stability of emulsion which depends on the rate of coalescence and also other important factors are the aggregation of the droplets, ionic strength, concentration, temperature, pH, energy, osmotic pressure, viscosity, interfacial tension and dynamically the addition of emulsifying agent (emulsifier), and stabilizer. The stability of emulsion depends on the steric hindrance and electrostatic interactions and the viscosity of the continuous phase (gelation) [6, 7]. The stability of the system is related to the empirical hydrophile–lipophile balance (HLB) number of the emulsion. [8]. Emulsifiers are small surface-active molecules and contain hydrophilic and hydrophobic areas, so they change the structure of the interface. They enhance its stability by reducing the interfacial tensions of dispersed phase-continuous phase (oil–water), and the van der Waals' steric and electrostatic repulsion have significant roles in stabilization [9]. Emulsifiers create special area for preventing them from aggregation and having low HLB value. Stabilizers are largely biopolymers (proteins, polysaccharides, phospholipids, plant-based emulsifiers) [10] and are amphiphilic molecules which contain hydrophobic and hydrophilic parts. Stabilizers decrease interfacial tension and conversely increase the surface area of immiscible phases. Synthetic surfactants and biosurfactants are two basic groups [11].

Emulsions can be classified according to the structure of the phases as single, multiple emulsions (a size range 0.1–5 μm), micellar emulsions, or micro-emulsions (a size range of 5–50 nm) and nano-emulsions (a size range of 10–500 nm). The single emulsion is a colloidal dispersion of two immiscible liquids (water and oil) and is simply divided into two systems as oil-in-water (O/W) or water-in-oil systems (W/O) depending on the dispersed phase (oil) or continuous phase (water) [12]. In W/O emulsions, simple steric effect is the key role for stabilizing the system, owing to the low electrical conductivity of the water (continuous phase) and their products can be in the solid or semi-solid and liquid forms. Studies about W/O emulsions investigate the interaction mechanisms of water, oil, and emulsifier (polarity, layer thickness, lipophilic bioactive compounds, and the charged molecules) and the emulsion stability for the development of new products and applications [13–17]. Sato et al. showed enhanced oxidation and pH stability as compared to systems produced with only one biopolymer in alginate-gelatin-mixed emulsions, and they explained the emulsifying properties of gelatin with the high pH resistance of alginate as a delivery system [18]. Roldan-Cruz et al. investigated the stability of O/W emulsion using Tween-80 as emulsifying agent [19]. Capitani et al. explained that in the O/W emulsion, polysaccharides (hydrophilic structure) increase the viscosity of the continuous phase, thereby decreasing the mobility of the oil droplets [20]. Nasrabadi et al. showed that the stability of emulsion improved by using linoleic acid (CLA), acacia gum (AG), and xanthan gum (XG) in oil-in-water emulsion. The experimental results discovered that a stable CLA emulsion can be used in beverage products [21]. Felix et al. focused on the preparation and stabilization of high-oleic O/W emulsions by using Xanthan Gum (XG) (0.06, 0.12, 0.25, and 0.50 wt.%) at different pH values (3.0, 5.0, and 8.0) [22]. Zhang et al. found that the droplet size and size distribution did not change throughout the storage by using the novel peptide-based nanoparticles as bifunctional and effective emulsifiers in O/W emulsion systems and the most important factors are well-controlled droplet size and composition [23]. Chang et al. also addressed a remarkable improvement in Fish oil-in-water emulsion stability due to the combined effect of thiol-modified β-lactoglobulin (β-LG) fibrils, chitosan, and maltodextrin by using a high-energy method [24].

Water-in-water (W/W) emulsions are much less known than classic oil-in-water emulsions and can be synthesized into two immiscible hydrophilic structures which are thermodynamically incompatible in solution. And also, the kinetic stability of W/W emulsions are mostly hard to control because amphiphilic molecules do not adsorb on emulsion interfaces. Nowdays, highly kinetically stable W/W emulsions can be prepared by using biocompatible and biodegradable ingredients [25].

Multiple emulsions are emulsions of emulsions and complicated polydispersed systems, which own extremely regular internal macromolecules and thus both oil-in-water-in-oil (O/W/O) and water-in-oil-in-water (W/O/W) emulsions exist simultaneously. The multiple emulsion is a complicated system such as water-in-oil-in water (W/O/W) or (O/W/O). Multiple emulsions are made up of small oil droplets dispersed in continuous phase (W) and are generally used in the different industrial sectors. (in food—slow release, in drug—the carrier, in cream—encapsulated compounds) [26]. W/O/W multiple emulsions occur in small water droplets intercepted within larger oil droplets that are themselves dispersed in a continuous phase [27]. Multiple emulsions have a

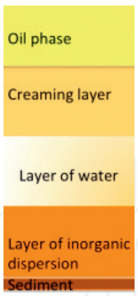
Formula	Definition		Ref.
$\frac{\eta-\eta_{\infty}}{\eta_0-\eta_{\infty}} = \frac{1}{\left(1+(\lambda\gamma)^2\right)^{d/2}}$	Zero shear viscosity	η_{∞}: infinite shear viscosity η: apparent viscosity λ: relaxation time d: power law index γ :: shear rate	[9]
$V_{(S)} = V_E(s) + V_{VDW}(s) + V_H(s) + V_{SR}(s)$	Interaction potential	$V_E(s)$: electrostatic potential $V_{VDW}(s)$: van der Waals potential $V_H(s)$ :: hydrophobic potential $V_{SR}(s)$ :: short-range interaction potential	[42]
$Yield = \frac{m_{w1}(t)}{m_{w1}(t_0)}$	Yield	$m_{w1}(t)$: the mass $m_{w1}(t_0)$: the initial mass	[43]
$\varphi = \frac{(\rho_{aq}-\rho_{em})}{(\rho_{aq}-\rho_{oil})}$	Volume fraction	ρ_{aq}: density of aqueous phase ρ_{em}: density of emulsion ρ_{oil}: density of oil	[44]
$EC(\%) = \frac{He\ (cm)}{Ht\ (cm)} x100$	Emulsifying capacity	He: Height of the emulsified layer (cm) Ht: Total height (cm)	[45]
$FC(\%) = \frac{Va-Vp}{Vp} x100$	Foam capacity	Va: Volume after agitation Vp: Volume prior to agitation	
$FS(\%) = \frac{Vr}{Vt} x100$	Foam stability	Vr: Residual foam volume Vt: Total foam volume	
$CI = \frac{Hc}{He} x100$	Creaming index 	He: the total height of the emulsion Hc: the height of the cream layer	[46, 47]
$EE = \frac{V\ encaps}{Vt} x100\%$	Encapsulation efficiency	Vencaps: the encapsulated oil Vtotal: the total volume of the oil phase	[48]
$EAI\left(\frac{m^2}{g}\right) = 2xTx\frac{A_0x\ N}{100000\ x\theta\ xL\ xC}$	Emulsifying activity index	A0: the absorbance at 0 min N: dilution factor q: is the proportion of the oil phase L: thickness of the cuvette (1 cm) C: the concentration of SPI (g/ mL)	[49]
$ESI\ (min) = \frac{A_0}{A_0-A_{10}} x(T_{10}-T_0)$	Emulsion stability index	A10: the absorbance at 10 min	

Table 1. The necessary calculations.

potent for droplet coalescence and for this reason alipophilic emulsifier (to stabilize the inner water in oil emulsion) and a hydrophilic emulsifier (to stabilize the outer oil in water emulsion) have key roles to disperse from one interface to the other [28–31].

3. Nano-emulsion systems

Nano-emulsion systems have smaller droplet sizes in the nanometric scale (mean droplet diameter ranges between 10 and 500 nm). Due to their small droplet size, they have different physicochemical properties and are thermodynamically unstable. Nano-emulsions are transparent and commonly prepared by using sonochemistry to produce smaller droplet sizes [32–35]. Ma et al. achieved the application of curcumin/triglyceride oil nano-emulsions to help improve solubility and bioavailability in food industry [36].

Pickering emulsions are known to spontaneously disperse small droplets of two immiscible liquids stabilized by solid nano- and micro-particles (silica, triacylglycerols, soft polymers, or clay) adsorbed at the interface. Pickering emulsions show excellent properties as to encapsulate any substance, to regulate the emulsion consistency by changing the solid concentration, and to get porous materials and special rheological behavior [37–40]. Dai et al. enhanced the stabilization of Pickering emulsion by using silica nanoparticles (SNP) in dimethyldodecylamine oxide (OA-12) and explained the dynamic behaviors of interface and the hydrophilic-lipophilic balance of particle surfaces [41]. Thus, from the information obtained in the literature, the necessary calculations for use in emulsion studies are given in **Table 1**.

Author details

Selcan Karakuş

Address all correspondence to: selcan@istanbul.edu.tr

Engineering Faculty, Chemistry Department, Istanbul University, Istanbul, Turkey

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