ARTICLE IN PRESS

CIS-01543; No of Pages 14

Advances in Colloid and Interface Science xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Advances in Colloid and Interface Science

journal homepage: www.elsevier.com/locate/cis

Historical Perspective

Silicone oil emulsions stabilized by polymers and solid particles

Masami Kawaguchi *

Division of Chemistry for Materials, Graduate School of Engineering, Mie University, 1577 Kurimamachiya, Tsu, Mie 514-8507, Japan

ARTICLE INFO

Available online xxxx

Keywords:
Silicone oil emulsions
Polymers
Solid particles
Solid particles with pre-adsorbed polymers
Emulsion stability
Rheological properties

ABSTRACT

Silicone oil emulsions stabilized by various emulsifiers such as polymers, solid particles alone, and solid particles with pre-adsorbed surfactants or polymers are reviewed, focusing on their emulsion stability and rheological properties as a function of the emulsifier concentration. An increase in the concentration of the emulsifier leads to a decrease in the droplet size and an increase in the emulsion stability, irrespective of the emulsifier. Moreover, the overlapping concentration of polymer can be regarded as a criterion for the preparation of emulsions using polymeric emulsifiers. Changes in the emulsion stability and rheological responses of the emulsions prepared by the solid particles with pre-adsorbed polymers are discussed in terms of the amounts of the emulsifiers adsorbed. For emulsions prepared from hydrophilic silica particles with pre-adsorbed polymers, a decrease in the droplet size of an order of magnitude can be controlled by an increase in the concentration of polymer, whereas hydrophilic silica particles alone cannot produce stable silicone oil emulsions.

Contents

---

* Tel.: +81 59 231 9432.
E-mail address: kawaguti@chem.mie-u.ac.jp.

http://dx.doi.org/10.1016/j.cis.2015.06.005
0001-8686/© 2015 Elsevier B.V. All rights reserved.

Please cite this article as: Kawaguchi M, Silicone oil emulsions stabilized by polymers and solid particles, Adv Colloid Interface Sci (2015), http://dx.doi.org/10.1016/j.cis.2015.06.005

1. Introduction

Simple and conventional emulsions prepared by traditional methods of stirring and shaking, i.e., dispersions of liquid (oil or water) droplets in a continuous liquid (water or oil) medium; can be considered to be unstable based on a simple thermodynamic idea using the Gibbs free energy change, ΔG, during emulsification. Emulsification at constant temperature, T, causes changes in both entropy, S, and interfacial area, A, such that ΔG is given by

$$\Delta G = \Delta H - \Delta ST + \gamma_{ow}\Delta A \tag{1}$$

where ΔH is the enthalpy change and γ_{ow} is the interfacial tension between oil and water. For emulsification, ΔH is almost zero. The term containing the interfacial area change, ΔA, is much larger than that containing the entropy change, ΔS, and thus ΔG is mainly attributed to γ_{ow} ΔA. A positive value of $\Delta G \approx \gamma_{ow}\, \Delta A$ implies that emulsions should be thermodynamically unstable. However, for systems that contain an emulsifier, the thermodynamics should be more complicated when the emulsifier is present at the interface. The emulsifier generally reduces the value of γ_{ow}, and thus the stability of the emulsion should be increased.

Four different processes are involved in the breakdown of a thermodynamically unstable emulsion, as shown in Fig. 1 [1]. Creaming and sedimentation processes occur in response to gravity, without changes in the size or size distribution of emulsion droplets. The flocculation process occurs when droplets come together to form aggregates, again without changes in either their size or size distribution. Ostwald ripening occurs in emulsions where the dispersed liquid has a limited solubility in the continuous liquid, so that larger droplets grow and smaller droplets shrink due to transport of the dispersed liquid between droplets through the continuous phase. Coalescence occurs by the merger of small droplets to form larger droplets, and often proceeds following the processes of creaming, sedimentation, and flocculation. Finally, two-phase separation occurs via Ostwald ripening or coalescence.

Since silicone oils, and specifically polydimethylsiloxane (PDMS), can be classified as typical hybrid organic/inorganic polymers, they show excellent performance as surface-active agents, decreasing the surface tension to values as low as 21 mN/m. They are insoluble in both water and polar organic solvents, and thus they are highly stable and chemically resistant. Moreover, they show strong powers of resistance to heating. Because of such properties, silicone oils have found applications in a diverse range of fields, including rubber, cosmetics, paints, inks, drug delivery, anti-former, and fabric care.

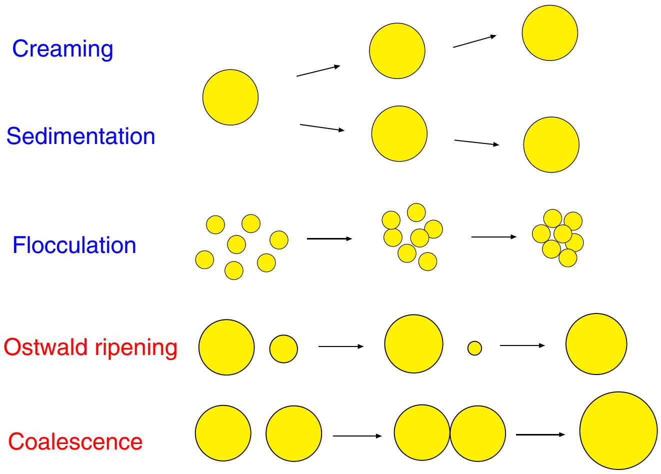

Fig. 1. Schematic representation of five different processes, such as creaming, sedimentation, flocculation, Ostwald ripening, and coalescence involved in the breakdown of a thermodynamically unstable emulsion.

Silicone oils have many applications as emulsions in water or organic solvents [1–3]. Such emulsions have generally been prepared by mechanically mixing the oil and emulsifier solutions in water and organic solvents, leading to the suppression of bubble formation in the continuous phase during the preparation process owing to the anti-former properties of the silicone oil. Surfactants, polymers, and solid particles have been used as emulsifiers for the preparation of silicone oil emulsions.

Since the preparation and stability of silicone oil emulsions are of considerable interest for technological, cosmetic, and pharmaceutical processes, it is important to understand them both from academic and technological points of view. This review article focuses mainly on the experimental studies performed in the last two decades, which address the effects of emulsifiers such as polymers and solid particles on the emulsion stability, and the interfacial and rheological properties of silicone oil emulsions dispersed in water.

2. Features of emulsions stabilized by polymers

Since polymeric emulsifiers, including synthetic and natural polymers, possess both hydrophilic and hydrophobic characteristics in their chains, and these properties are well in valance, they should provide a better emulsion stabilization than monomeric surfactants due to their stronger adsorption abilities [4,5]. However, the use of low-molecular-weight surfactants as emulsifiers induces adsorption with a single anchoring point at an interface. This allows the corresponding emulsifiers to be easily desorbed from the interface, which enhances phase separation. Conversely, high-molecular-mass emulsifiers such as linear polymers are advantageously attached to an interface by some segments, and form a thick adsorbed layer with a loop–train–tail conformation [5]. Since the adsorption of polymer chains is often less reversible, effective adsorption occurs even at low polymer concentrations, and the adsorbed chains cannot be easily desorbed from the interface.

It is well known that the stability of emulsions prepared by low-molecular-weight surfactants strongly depends on their concentration: above their critical micelle concentration (cmc) the emulsions are stable, whereas below the cmc they gradually coalescence [1]. However, there are no established criteria for the effect of concentration change on emulsion stabilization for polymeric emulsifiers. The overlapping concentration, (C^*) [6], may act as a criterion for the preparation of emulsions stabilized by polymeric emulsifiers, since polymer chains in bulk solutions above C^* cause chain entanglements, which form a sterically protective and thick adsorbed layer. In such preparations, the polymer concentrations used are generally around or above C^*. Furthermore, when the free-polymer concentration in the continuous phase is above C^*, not only the free-polymer chains in bulk but also the adsorbed polymer chains may easily provide chain entanglements with the corresponding free-polymer chains, leading to the stronger stabilization of emulsions.

3. Features of emulsions stabilized by solid particles

The first sytematic study of the stabilization of paraffin oil droplets in water by solid particles in the absence of surfactants was made by Pickering in 1907 [7], who examined several types of solid particle. Since then, many works on emulsions stabilized by solid particles have been reported. These have been summarized in some reviews and textbooks, and the corresponding emulsions have been widely referred to as Pickering emulsions [8]. Developments in the study of Pickering emulsions have also been greatly indebted to an important idea proposed by Schulman and Leja [9], who linked the contact angle of the solid particle between oil and water with the emulsion stability.

Fig. 2 represents the typical contact angle, θ, of a spherical hydrophilic or hydrophobic particle between oil and water. For hydrophilic particles, values of θ are less than 90°, whereas for hydrophobic particles they

Please cite this article as: Kawaguchi M, Silicone oil emulsions stabilized by polymers and solid particles, Adv Colloid Interface Sci (2015), http://dx.doi.org/10.1016/j.cis.2015.06.005