Stabilization of Pickering Emulsion using Micro and Nano Silica Particles

Bansi B. Kariya[1], Piyush B. Vanzara[2], Divya K. Rajput[3]
[1, 2, 3] Department of Chemical Engineering
[1, 2, 3] V.V.P. Engineering College, Rajkot

Abstract- *The phenomenon that solid particles that can reside at the interface of bubbles and droplets, thereby providing them resistance against the coalescence and Ostwald ripening, is known as the Pickering emulsion (Pickering, 1907). Here we stabilized Pickering emulsion with silica nano particles as well as micro particles and study the Pickering emulsion stability at two different temperatures with time. We observed different emulsions that are liquid stabilized emulsion and solid stabilized emulsion- Pickering emulsion, and mixed emulsifier emulsion- prepared using liquid stabilized emulsion as well as solid stabilized emulsion with varying composition of solid and liquid stabilizers at two different temperature. The mixed emulsifier emulsion show higher stability at lower temperature and this can be also proved by particle size analysis.*

Keywords- Pickering emulsion, Stabilization, Nano silica, Emulsifier, Piranha Solution, O/W emulsion

I. INTRODUCTION

Emulsion is a fine dispersion of minute droplets of one liquid into other which is not soluble and is encountered in products including foods, cosmetics, and pharmaceuticals. A proper formulation of an emulsion will ensure its stability against droplet coalescence and macroscopic phase separation. This is normally accomplished with the addition of amphiphilic molecules, such as surfactants that lower the interfacial tension of the liquid/liquid interface.[1] The ability of solid particles to adhere to soft deformable interfaces, for example to the surface of emulsion droplets or bubbles, is currently the subject of renewed interest in material science. The phenomenon that solid particles can reside at the interface of droplets and bubbles, thereby providing them with resistance against coalescence or fusion, and (debatable) coarsening or Ostwald ripening, is known as Pickering stabilization and named after Spencer Umfreville Pickering.[2]

Food science and flotation technology show a steady stream of research over the 20th century using Pickering stabilization. Interestingly, the origins of Pickering stabilization in the area of (froth) flotation lie further back than the cited works by Pickering (1907) and Ramsden (1903)[2-3]. In the area of polymer chemistry the idea of using solid particles as stabilizers for the fabrication of polymer beads by suspension polymerization was explored to some extent from the 1930s to the 1950s[4-6]. A revival of the concept of using solid particles as stabilizers in heterogeneous polymerizations did not emerge until 50 years later with the development of Pickering mini-emulsion polymerization[7-9] and Pickering emulsion polymerization.[10-12] The idea of using Pickering stabilization as a way of assembling colloidal particles into intricate supracolloidal structures drew attention from the soft matter physics crowd initiated by the works of Velev et al.[13-15] and Dinsmore and coworkers,[16] the latter coining the term 'colloidosomes' for the semi-permeable hollow structures made by assembly of particles onto droplets. Not only does the fabrication of supracolloidal structures receive great attention, but also the underlying physics is studied and discussed widely, for example looking at why particles adhere to a liquid–liquid interface, how strong the interaction energy is, and what the interplay between particles at the droplet surface is. The question of why a particle would prefer to sit at the interface of an emulsion droplet instead of being dispersed in either the water or oil phase has already been raised and discussed by Hildebrand and coworkers in 1923.[17] They said that for solid particles to adhere to and be collected at the surface of emulsion droplets, the powder had to be wetted by both liquids. They stated that in general particles have a preference for one of the two liquids, which meant that the particles would reside for longer in that liquid. They described how the assembly of particles onto the oil–water interface will cause the interface to bend in the direction of the more poorly wetting liquid, thereby facilitating its emulsification into droplets. They concluded that the type of emulsion, i.e. oil-in-water or water-in-oil, could be predicted on the basis of this wet ability, and thus on the basis of the contact angle of the interface with the solid.

II. EXPERIMENT SECTION

Chemicals Required: Fused Silica ranging 85-100 nm (Evonik Industries, AEROSIL ® R816), Fused Silica 200 mesh size (Buntrock International Pvt. Ltd.) Paraffin Wax (SD Fine Chem Limited), Tween 80 (SD Fine Chem Limited), Methanol 99% (SD Fine Chem Limited),

Hydrogen Peroxide H_2O_2 30% AR (SD Fine Chem Limited), Sulfuric Acid 98% (SD Fine Chem Limited)

Preparation of Pickering Emulsion

Piranha Solution Preparation: Piranha solution is prepared by using hydrogen peroxide (30%) and Sulfuric acid [3:1], in that 10 ml of Hydrogen Peroxide is taken in which drop wise addition of sulfuric acid (approximately 15ml) was made, such that the solution starts boiling, as process is highly exothermic.

Pretreatment of Silica with Piranha Solution: 0.2 grams of fused silica particles of 400 mesh size was taken. Piranha was added in the solution and kept for a while and allowed it react with the surface of silica particles, this leads to hydroxylation of the silica particles surface.

Then it was centrifuged for 10 minutes at 5000 rpm. The process was repeated since the particles were not completely settled on the bottom. Pre treated fused silica particles were dried under vacuum at 85^0C for a continuous span of time. Since both the hydrogen Peroxide and Sulfuric acid were highly hydrophobic, use of desecrator had been conducted.

Pure Pickering Emulsion: Initially silica-in-wax dispersions were prepared at the required temperature of 75^oC, where silica was added in the carefully weighted quantity of paraffin (oil phase). The silica-in-wax dispersion was then added to 30 ml quantity of water and the mixture was emulsified with the high shear magnetic stirrer.

Surfactant Stabilized Emulsion: Tween80 was added to the distilled water and gently agitated at 75°C until dissolved. The paraffin wax (oil phase), kept at a constant temperature of 75^oC, and was then added to distilled water and surfactant solution, the mixture was emulsified with the high shear mixer.

Mixed Emulsifier Emulsion: Mixed-emulsifier emulsions were prepared in the presence of both Tween80 and hydrophilic silica particles. Silica was added in the oil phase and Tween80 was added in the water phase then they were agitated at high shear at 75^oC. Different samples were prepared by varying the amount of surfactant and silica.
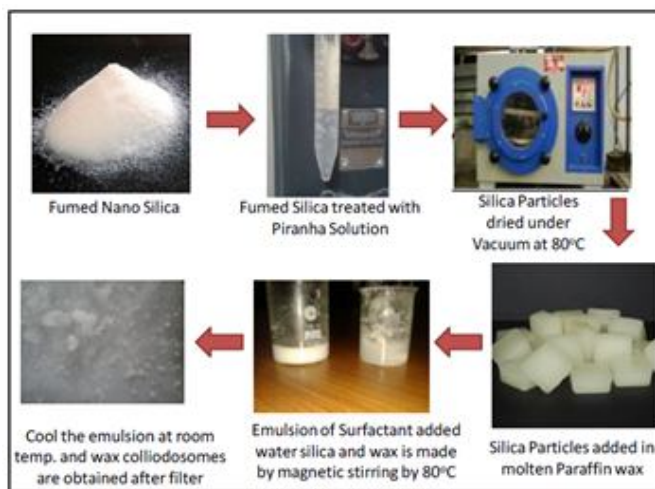

Fig. 1 Experimental Procedure approached in Pickering Emulsion

Characterization

Particle Size Analysis was used to determine silica size using Malvern Nanosight-(NTA NTA .1Build 3.1.54) particle size analyzer.

Particle size Analysis was used to determine distribution in diluted emulsion system using Microtrac Particle size analyzer-NPA152.

Scanning Electron Microscopy (SEM) was used to image the colloidosomes obtained from emulsion. Prior to imaging, a thin layer of platinum was evaporated onto them to render them electrically conductive, avoiding the surface charging the electron beam.

III. RESULT AND DISCUSSION

Particle Size Analysis of fused Nano Silica: The interest in Pickering emulsion, i.e. emulsion stabilized by solid particles, has increased in last two - three decades. The mechanisms involved in emulsion stabilization have been investigated. The ability of solid particles to stabilize Pickering emulsion depend on water and oil properties as well as solid particles properties themselves. Fused silica is a non-crystalline form of silicon dioxide (SiO_2). Usually they are suspended in an aqueous phase that is stabilized electrostatically. Density of fused silica was 2.2 g/cm3. The particle size of nano silica particles is 85 nm, can be analyzed using laser diffraction particle size analyzer is shown in figure 2.
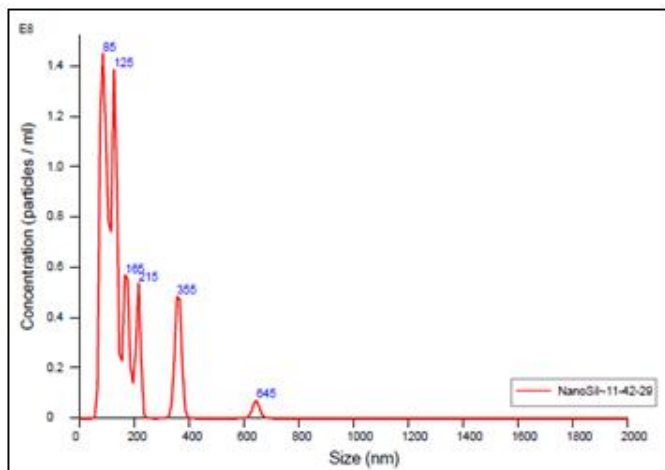
Fig. 2 Particle size analysis of fused nano silica particles

O/W Pickering Emulsion Stability with nano silica: To study the effect of silica, surfactant and both silica and surfactant on the stability of emulsion.

Table 1 Study of effect of surfactant on emulsion with nano silica at different composition

Sample	Pretreated Silica (gm)	Tween 80 (ml)	First visible interface at 30°C (min)	First visible interface at 30°C (min)	Final separation resulting in compressed emulsion state	
					At 10°C	At 30°C
A	0	0	1.5	1	3	2
B	0.4	0	5	3	150	120
C	0.4	1	24	18	8 h	5.5 h
D	0.4	2	30	25	10 h	8.5 h
E	0.4	3	18	12	5.5 h	4 h
F	0.3	2	19	14	6 h	5 h
G	0.5	2	23	17	7.5 h	4 h
H	0.6	2	28	23	8 h	6 h
Paraffin Wax (5 gm), Water (30 ml)						

O/W emulsions were prepared using water and paraffin wax with a fixed amount of silica and varying amount of silica and surfactant (Tween 80). Silica particles of size 85 nm were used for preparing these emulsions. Seven sets of emulsions were prepared by providing high shear at 75°C were allowed to cool down at two different temperatures 10°C and 30°C. The effect of addition of surfactant and silica on the stability of emulsion at two temperatures 10°C and 30°C is shown in table 1.

The first series of experiments (Sample A) were conducted without addition of silica and surfactant; this predicted the actual stability of oil in water emulsion. The second series of experiments were conducted with addition of

0.4 gm silica (sample B) without addition of surfactant and possible stability offered by silica particles was observed. The other three series of samples C, D, and E were conducted using fixed amount of (0.4 gm) silica particles and by varying amount of surfactant added. The remaining series of samples F, G and H were conducted using fix amount of surfactant (2 ml) and by varying amount of silica particles.

Figure 3 shows the emulsion stability at two temperatures with time. The phase separation was observed with time until it reached compressed stage. The sample which is stored at lower temperature stays stable for a longer time than that stored at higher temperature. The interface obtained at different temperature also gives us idea of emulsion composition selection. From figure 3, the effect of surfactant on emulsion stability can be well understood at two temperature 10°C and 30°C with time.
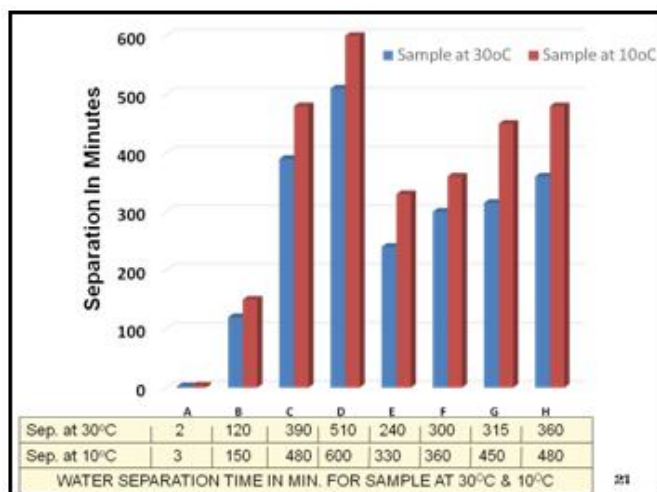

Fig 3 Study of emulsion stability with time until it reached the compressed stage at 30°C and 10°C

O/W Pickering Emulsion Stability with Micro Silica: Seven sets of emulsions were prepared by providing high shear at 75°C were allowed to cool down at two different temperatures 45°C and 25°C.The effect of addition of surfactant and silica on the stability of emulsion at two temperatures 45°C and 25°C is shown in Table 2.

The first series of experiments (sample A) were conducted without the addition of silica and surfactant; this predicted the actual stability of oil in water emulsion. The second series of experiments were conducted with the addition of 0.2 gm silica (sample B) without the addition of surfactant and the possible stability offered by silica particles was observed.

The remaining series of experiments were conducted using fixed amount of (0.2 gram) silica particles and by

varying the amount of surfactant added (sample C, D, E, F and G). Figure 4 shows the emulsion stability at two temperatures with time.

Table 2 Study of effect of surfactant on emulsion with micro silica at different composition

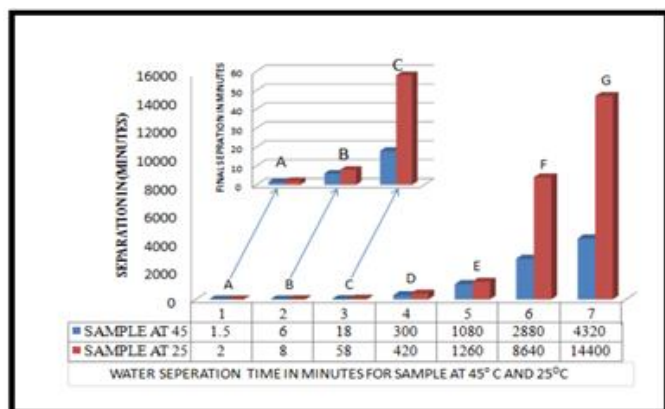| Sample	Pretreated Silica (gm)	Tween 80 (ml)	First visible interface at 45°C (min)	First visible interface at 25°C (min)	Final separation resulting in compressed emulsion state	
					At 45°C	At 25°C
A	0	0	1	1.5	1.5	2
B	0.2	0	2	3	6	8
C	0.2	1	6	8	18	58
D	0.2	2	10	12	5 h	7 h
E	0.2	3	24	55	18 h	40 h
F	0.2	4	4 h	6 h	48 h	144h
G	0.2	5	13 h	16 h	72 h	240 h
Paraffin Wax (2 gm), Water (10 ml)						

Fig 4 Study of emulsion with time until it reached the compressed stage at 45°C and 25°C

The phase separation was observed with time until it reached the compressed stage. The samples which are stored at low temperature stay stable for a longer time than that stored at higher temperature. The interface obtained at different temperatures also gives us idea of emulsion composition selection. From Figure 4, the effect of surfactant on emulsion stability can be well understood at two temperature 45°C and 25°C with time, an extended column graph of sample A, B and C is also shown inside it.

Liquids or suspensions as consisting of particles which move very slowly compared to gases, there comes a point where all particles are in close contact with one another and therefore experience structural arrest. In the sample emulsions system prepared, the final stage represents the stage, where there is no kinetics energy of consequence.

The typical energy required to change position of jammed droplets is very large compared to thermal energy at room temperature. The compressed emulsions stage can be stable with coalescence and Oswald ripening for months and years depending on emulsion system.

Effect of internal droplet size on stability of Emulsion: The internal droplet size of emulsions was measured using a Microtrac Particle size analyzer- NPA152. Two emulsions were prepared, with 2 ml surfactant using 0.4 gm silica. These emulsions were kept for 30 days to study the effect of time on internal drop size distribution of the emulsions. The particle size analysis of fresh sample and aged sample was carried out.

Figure 5 shows the changes that occurred in particle size distribution for emulsion with silica particles. It can be seen that a bimodal size distribution is observed for the emulsion after 30 days. Most of the part of distribution superimposes with that of silica particles indicating the involvement of only a few silica particles in emulsion stability and other must have settled down as excess silica. Figure also shows the comparison between the fresh sample and the emulsion after 30 days. It can be seen that emulsions move towards its instability because of Oswald ripening and creaming with time.
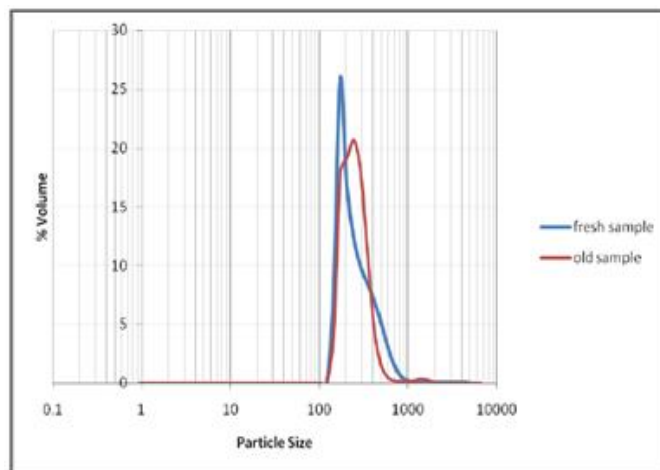

Fig 5 Comparison of fresh and 30 days older emulsion sample

Microscopy of Colloidosomes: Figure 6 shows the SEM image of Colloidosomes which indicate that silica particles are adsorbed to wax to form Colloidosomes. Wax Colloidosomes starts to agglomerate as the emulsion is diluted and kept for filtration. After the Colloidosomes cooling to room temperature which involved some disruptive volume compression of wax phase, the monolayer surface coverage remained high. As oil phase solidified to wax, particles were locked at interface of wax and ceased to rotate, so further modification can be possible.
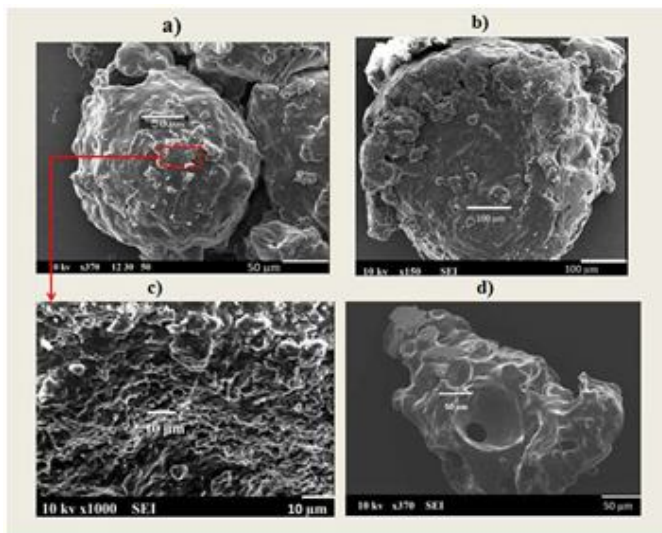
Fig 6 a) and b) SEM images of Colloidosomes c) Magnified SEM image of (a) at x1000 d) SEM image of colloidosomes when methanol was added during filtration.
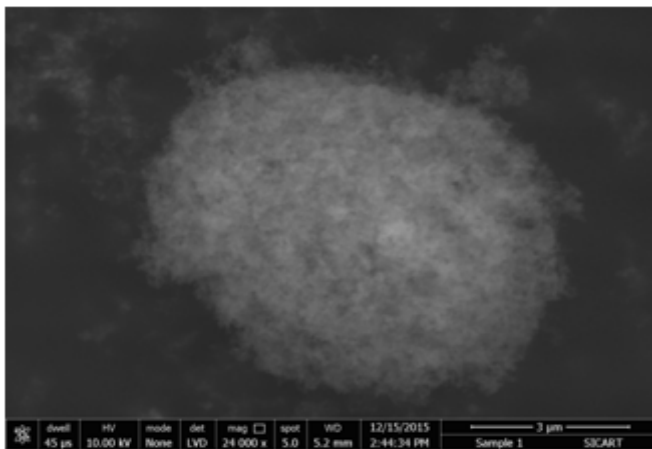

Fig 7 SEM image of Colloidosomes with nano silica

IV. CONCLUSION

It can be conclude that at the lower temperature, the stability of the Pickering emulsion is more than the stability observed at the higher temperature, and by using the emulsifier for the formation of the Pickering emulsion, the stability can be increased with varying quantity of the nano silica with the surfactant and also we noticed that the stability of Pickering emulsion is higher with nano silica particles than that with micro silica particles.

High temperature develops better condition for the Ostwald ripening that result into breakdown of the emulsion. The amount of the surfactant should be preciously used otherwise the surfactant has ability to stabilize the emulsion by its own so the proper composition of the surfactant with nano silica in paraffin wax and water system should be known, for this system the composition used for the stabilizing the

Pickering emulsion with contribution of both silica and surfactant is 2 ml Tween 80 and 4 gm nano silica in the system of 5 gm paraffin wax and 50 ml water system.

REFERENCES

[1] Binks, B. P.; Curr. Opin.; "Particles as surfactants-similarities and differences"; Colloid Interf. Sci. 2002, 7, pp 21–41

[2] S.U. Pickering, "Emulsions" J. Chem. Soc., 1907, 91, pp 2001-2021

[3] Ramsden, W., "Separation of solids in the surface-layers of solutions and 'suspensions' (observations on surface-membranes, bubbles, emulsions, and mechanical coagulation", Phil. Trans. R. Soc. London, 1903, 72, pp 156-164

[4] von E. Trommsdorff, "Über Perlpolymerisation", Macromolecular Chemistry and Physics, 1954, 13(1), pp 76-89

[5] O. RÖhm and E. Trommsdorff, "Process for the polymerization of methyl methacrylate" US 2171765 A, 1939

[6] W. P. Hohenstein, "Suspension polymerization of vinyl compounds" US 2524627 A, 1950.

[7] Séverine Cauvin , Patrick J. Colver , and Stefan A. F. Bon, "Pickering Stabilized Miniemulsion Polymerization: Preparation of Clay Armored Latexes" Macromolecules, 2005, 38 (19), pp 7887–7889.

[8] Stefan A. F. Bon and Patrick J. Colver, "Pickering Miniemulsion Polymerization Using Laponite Clay as a Stabilizer", Langmuir, 2007, 23 (16), pp 8316–8322

[9] Sara Fortuna, Catheline A. L. Colard, Alessandro Troisi and Stefan A. F. Bon, "Packing Patterns of Silica Nanoparticles on Surfaces of Armored Polystyrene Latex Particles", Langmuir, 2009, 25 (21), pp 12399–12403

[10] Patrick J. Colver, Catheline A. L. Colard and Stefan A. F. Bon, "Multilayered Nanocomposite Polymer Colloids Using Emulsion Polymerization Stabilized by Solid Particles", J. Am. Chem. Soc., 2008, 130 (50), pp 16850–16851

[11] Catheline A. L. Colard, Roberto F. A. Teixeira and Stefan A. F. Bon*, "Unraveling Mechanistic Events in

Solids-Stabilized Emulsion Polymerization by Monitoring the Concentration of Nanoparticles in the Water Phase", Langmuir, 2010, 26 (11), pp 7915–7921

[12]   Roberto F. A. Teixeira, Holly S. McKenzie, Ashton A. Boyd, and Stefan A. F. Bon*, "Pickering Emulsion Polymerization Using Laponite Clay as Stabilizer To Prepare Armored "Soft" Polymer Latexes", Macromolecules, 2011, 44 (18), pp 7415–7422

[13]   O. D. Velev ,*† K. Furusawa ,‡ and K. Nagayama, "Assembly of Latex Particles by Using Emulsion Droplets as Templates. 1. Microstructured Hollow Spheres", Langmuir, 1996, 12 (10), pp 2374–2384

[14]   O. D. Velev ,*† K. Furusawa ,‡ and K. Nagayama, "Assembly of Latex Particles by Using Emulsion Droplets as Templates. 2. Ball-like and Composite Aggregates", Langmuir, 1996, 12 (10), pp 2385–2391

[15]   O. D. Velev *† and K. Nagayama, "Assembly of Latex Particles by Using Emulsion Droplets. 3. Reverse (Water in Oil) System", Langmuir, 1997, 13 (6), pp 1856–1859

[16]   A. D. Dinsmore, Ming F. Hsu, M. G. Nikolaides, Manuel Marquez, A. R. Bausch, D. A. Weitz, "Colloidosomes: Selectively Permeable Capsules Composed of Colloidal Particles", Science, 2002, 198(5595), pp 1006-1009

[17]   Philip Finkle, Hal D. Draper, Joel H. Hildebrand, "the theory of emulsification", J. Am. Chem. Soc., 1923, 45 (12), pp 2780–2788