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ORIGINAL ARTICLE

Three-phase surfactant-less emulsions

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Abstract Two emulsions were prepared of water, silicone oil (SO) and vegetable oil (VO) with 1:3 ratio of SO and VO, and different amount of water, and investigated for destabilization mechanisms. The emulsions were highly unstable with no mutual solubility between the three liquids and with the absence of surfactant and the investigation focused on a combination of coalescence and sedimentation/creaming processes.

With no water present, the system was only of the type VO/SO single emulsion, while with water present two types of emulsions were formed.

1. Introduction

Emulsions are unquestionably among the most important of all the colloid and macro-dispersed systems not only from a commercial point of view, but also of their great interest scientifically (Binks, 1998; Sjoblom, 2006; Aserine, 2008; Leal-Calderon et al., 2007; Tadros, 2009). They are prevalent in foods as illustrated by a number of monographs over the years (Peleg and Bagley, 1983; Bee et al., 1989; Friberg et al., 2004; McClements, 2005) and in cosmetics and personal care in general (Rhein et al., 2006; Tadros, 2008) and pharmaceutics (Niellod and Marti-mestres, 2000).

Emulsions are frequently characterized by their "stability", by which is meant the rate of destabilization, of which the primary processes of flocculation and coalescence have earlier been extensively analyzed (Wasan and Nikolov, 2001; Dukhin et al., 2001), with recent breakthroughs (Bremond et al., 2008; Grimes et al., 2010).

In parallel with these two initial processes, gravitational forces also cause creaming/sedimentation to take place (Bibette et al., 1992; Dickinson and Ritzoulis, 2000) and for emulsions with long term stability the Ostwald ripening (Taylor, 1995; Kabalnov and Shchukin, 1992; Mun and McClements, 2006). Recent contributions have attempted a unifying approach to these processes (Pasalic et al., 2007; Urbina-Villalba, 2009).

One of the different classes of emulsions is the double emulsions in which compound **A** is emulsified into compound **B**, and the resulting emulsion in turn is emulsified into **A**, forming **A**/**B**/**A** dispersions that were initially prepared in this manner

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(Matsumoto et al., 1976). The emulsions have attracted pronounced interest over the years with Garti as the leading researcher (Garti and Aserini, 1996; Menon and Wasan, 1988; Pala, 2007). Aveyard earlier introduced a one-step method to prepare double emulsions using stabilization by two kinds of solid particles with slightly different wettability (Aveyard et al., 2003). Finally Rocha-Filho and collaborators introduced and investigated one step processes with traditional surfactants (Jacqueline et al., 2008). Microfluidics of two liquids heptadecafluoro-1,1,2,2-tetrahydrodecyl triethoxy-silane and a combination of tetraethylorthosilicate and methyltriethoxysilane were used to prepare double dispersions of homopolymers (Chia-Hung et al., 2009).

The introduction of microfluidic devices to prepare double emulsions represented a second break through for double emulsions. Early review articles described the conditions of the method (Nisisako et al., 2005). Weitz and collaborators have become the leading researchers formulating a long series of complex multiple emulsions and particles (Chen et al., 2009; Shum et al., 2010; Muschiolika, 2007; Ahn et al., 2006). This method is both elegant and efficient and is only limited by the capacity limitation to kg day^{-1}. Nevertheless it was the only avenue, except using pegylated oils (Jorgensen and Nielsen, 2010) to obtain Janus emulsions of two oils till Hasinovic and Friberg recently found a bulk method (Hasinovic and Friberg, 2011) indicating a realistic avenue for further progress. Nevertheless, the method is obviously still in the primary discovery state and needs fundamental studies in order to establish a sound and reliable basis for further development. The process clearly depends on the mutual interfacial free energies of the liquids and the authors found a fundamental investigation into such effects to be useful in order to clarify the fundamentals of such systems. In the present contribution an emulsion of three liquids with virtually no mutual solubility was investigated for destabilization mechanisms. Since no surfactant is included the emulsion is extremely unstable and the investigation could focus on the coalescence and sedimentation/creaming processes.

2. Experimental

2.1. Materials

Silicone oil (SO) (dimethyl poly siloxane, 100 CST) was obtained from acros. Vegetable oil (VO) (extra virgin cold first press olive oil) was obtained from Integrated Olive Products Co., Ltd. Both oils were used without further purification. Water (W) was deionized and distilled.

2.2. Instrumentation

Weights were determined using a Mettler AJ150 Analytic Balance. SlectA Movil-Tub Plate shaker was used for overnight emulsification. VT-T-PC MEIJI inverted microscope was used for the formed emulsions microphotographs with a magnification of 10 × 10 (100).

2.3. Emulsions preparation

Four-gram emulsion samples with 1:3 ratio between silicone oil (SO) and vegetable oil (VO) with different amounts of water added. The water was poured into a 1-cm diameter flat-bottomed test tube without sepreading along the glass. The SO was carefully poured on top of the water layer forming a distinct interface. Finally the VO was poured on top of the SO, forming a second distinct interface.

Table 1 Emulsion composition.

Emulsion	X_W	X_{VO}	X_{SO}
1	0	0.750	0.250
2	0.100	0.675	0.225

The height of each layer and the total height were measured, and the samples emulsified in two stages. In the first stage, the samples were left for overnight at the plate shaker, in the second stage, the samples were emulsified by turning the test tube upside down 25-times. The destabilization was followed by measuring the changes in the total height, the height of formed emulsions, the height of separated layers, of VO, SO, W and of the emulsion.

The emulsion compositions are written as weight fraction as shown in Table 1, in which X_w denotes the weight fraction of water, X_{VO} the weight fraction of vegetable oil, and X_{SO} the weight fraction for the silicone oil.

2.4. Samples for micro-photo

Three additional samples from emulsion two were prepared and emulsifeid in the previous manner, and the formed emulsions samples were microphotographed at different times.

3. Results

An overview of the destabilization of emulsion (0, 0.75, and 0.25) is given in Fig. 1 revealing some essential features. The freshly prepared emulsion evidently was of the VO/SO kind, in spite of the opposite ratio 3/1 between the two compounds. This conclusion is proven by the interface in the emulsion after 10 min (Fig. 1). The process gave rise to two separated layers of pure compounds with dissimilar origin, as exemplified by the two layers appearing in the emulsion after 10 min (Fig. 1). The top layer, VO, was formed after creaming and coalescence of VO drops in the lower VO/SO emulsion, while the SO layer beneath the latter emulsion was the continuous phase of the VO, appearing because of the rise of the VO drops.

The layer dimensions are given in Fig. 2 as the emulsion and the VO liquid volume fractions. In addition the lower transparent layer as part of the SO emulsion is shown.

The features in Fig. 2 are notable for two reasons. At first there is an induction time of 5 min for the separation of VO and the appearance of the transparent SO layer. The delay of the separation of the VO layer is a consequence of parallel coalescence and creaming. During the first minutes only coalescence took place as revealed by the photograph of the test tube in Fig. 1 after 5 min, showing large VO drops within the emulsion. The size of these drops increases as demonstrated by the photograph after 10 min. In spite of the pronounced variation in the drop size according to Fig. 1, the separation rates for the both the VO and SO layers were remarkably constant for extended periods of time, as evidenced by the equations in Table 2.

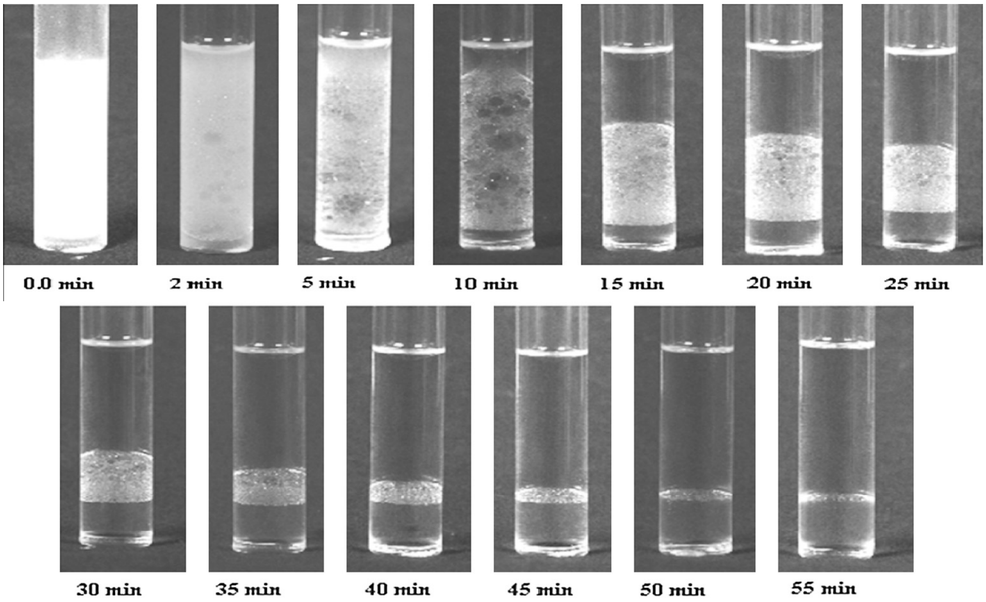

Figure 1 The layers in emulsion (0, 0.75, and 0.25) at different times.

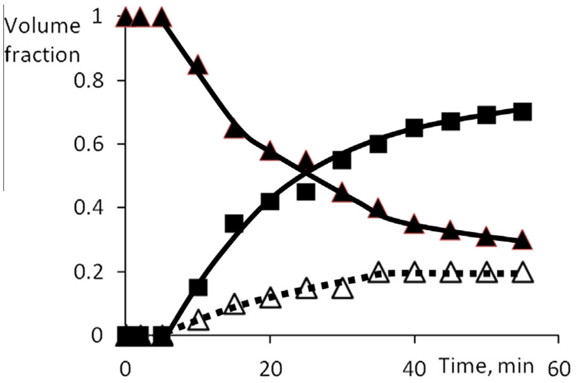

Figure 2 The volume fraction of the emulsion (0, 0.75, and 0.25) versus time. ■, Separated VO; ▲, SO emulsion; △, transparent layer within the SO emulsion.

Although it would be appealing to find a fundamental basis for constant rates, the phenomenon must be judged as fortuitous, because the SO continuous emulsion is of the high internal ratio kind and any attempt to describe it in term of drops rising through a continuous medium is unrealistic. The correct illustration of the process will be given in the Section 4. Nevertheless, the results per se are the foundation for the second feature; the weight fraction of VO within the turbid part of the SO emulsion layer in Fig. 1. This fraction was calculated in the following manner. The volume fractions underlying Fig. 2 and Table 3, were used to calculate the weights of the SO and VO layers. Knowing the total weight of each of the two compounds from the emulsion composition, their weights in the emulsion layer were obtained by subtraction and the weight fraction of VO in the emulsion computed, last column in Table 3. The numbers are remarkable in being constant to a high degree; a relationship indicated by the similarity of the curves for the volume fraction of VO and transparent SO in Fig. 1. The fundamental reason for this behavior will be outlined under the Section 4.

The overview of the destabilization for the emulsion (0.100, 0.675, and 0.225) is given in Fig. 3 with features quite similar to those in Fig. 1, except for the fact that the top VO layer is less transparent.

The differences in the behavior are apparent first in the diagram of layer dimensions versus time (Fig. 4). In the diagram for the emulsion (0.1, 0.675, and 0.225) the readings after 30 min were constant and have not been included in order to emphasize the essential features. For the same reason the values for the separating water layer reaching approximately linearly to 0.1 at 30 min was excluded.

The critical feature in Fig. 4 is a fact that the emulsion with water is less stable; a feature that would be even more accentuated, if the fractions were counted only on the two oils. The emulsion with water does not only separate the VO more rapidly, the creaming of the VO drops within the SO emulsion is faster as illustrated by smaller fraction of the bottom transparent layer of the emulsion. At 20 min this layer in the

Table 2 Equations for the dimension fractions versus time.

Time span (min)	Dimension fractions, equations	
	VO	SO
5–15	0.35t – 0.183; (R^2 = 0.993)	0.01t – 0.05; (R^2 = 1.00)
15–40	0.126t + 0.159; (R^2 = 0.980)	0.0046t + 0.029; (R^2 = 0.93)
40–55	0.0034 + 0.516; (R^2 = 0.980)	0.2; (R^2 = 1.00)

Table 3 Volume fractions and calculated weights of the VO and SO layers as well as the weight fraction of VO in the emulsion layer.

t	Volume fractions			Weights		VO/(VO + SO)
	VO	SO	E	VO	SO	
0	0	0	1	0	0	0.77
2	0	0	1	0	0	0.77
5	0	0	1	0	0	0.77
10	0.15	0.05	0.8	0.134	0.049	0.78
15	0.35	0.1	0.55	0.313	0.098	0.77
20	0.42	0.12	0.46	0.375	0.117	0.78
25	0.45	0.15	0.4	0.402	0.146	0.82
30	0.55	0.15	0.3	0.491	0.146	0.77
35	0.6	0.2	0.2	0.536	0.195	0.88
40	0.65	0.2	0.15	0.580	0.195	0.85
45	0.67	0.2	0.13	0.598	0.195	0.83
50	0.69	0.2	0.11	0.616	0.195	0.82
55	0.7	0.2	0.1	0.625	0.195	0.81

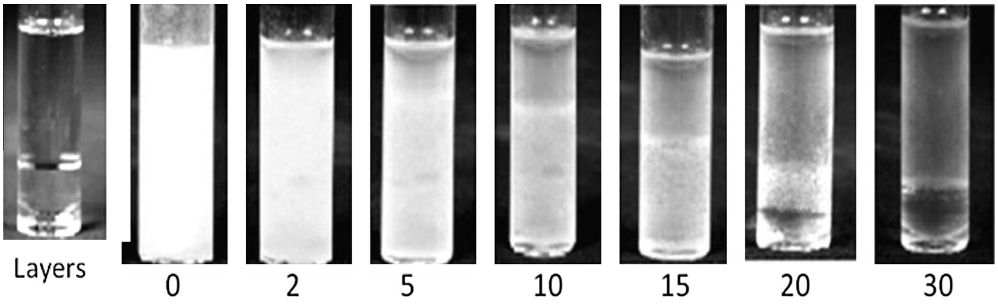

Figure 3 The layers in emulsion (0.1, 0.675, and 0.225) at different times.

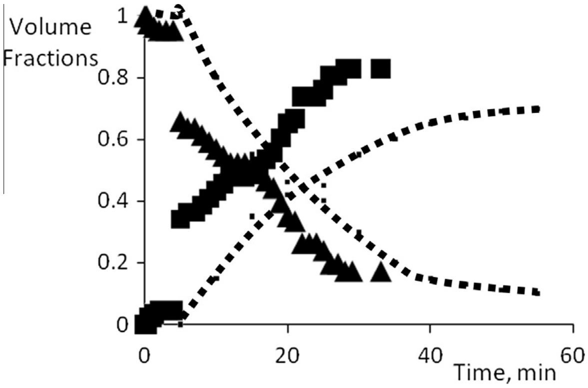

Figure 4 The volume fraction of the emulsion (0.1, 0.675, and 0.225) versus time. ■, Separated VO; ▲, SO emulsion; the dotted lines are the values from Fig. 2.

waterless emulsion occupies 20 vol.%, but 40% in the emulsion with water. The initial condition in the system with no water is a single emulsion, VO/SO, while this is not the case for the system with water. For that emulsion the volume fractions from 5 to 33 min give straight lines extrapolating to volume fractions of the VO and SO emulsions as, respectively, 0.22 and 0.78, a strong indication of two initial emulsions of which the SO one occupies the largest fraction. Considering these differences information about the drop size and configuration is useful and necessary. Microscopy photos of the water less emulsion showed only single drops as expected, but so did also the (0.1, 0.675, and 0.225) emulsion (Fig. 5).

The original emulsion, Fig. 5 left, is characterized by a wide distribution of drop sizes from a maximum of 70.8 μm to drops with a diameter less than 1.6 μm. The VO drops in the SO emulsion closely beneath the VO emulsion layer after 20 minutes of storage, Fig. 5 middle, shows a similar size distribution and a number of flocculated drops. Conversely, the drops in the lower part of the SO emulsion, Fig. 5 right, shows no extremely large drops and no flocculated ones.

4. Discussion

The results rest on two fundamental phenomena; the relationship between interfacial free energies versus the configuration of the emulsions and the destabilization processes of the emulsions. The foundation for the first item; is available as numerical values for the interfacial tensions with the vegetable oil/water interfacial tension recently evaluated and found to be in the range of 23–26 mN/m (Fisher et al., 2006), while the interfacial tension between water and silicone oils varies considerably with the presence of polar groups in the latter, but a contemporary publication (El-Hamouz, 2007) gives the interfacial tension of 42 mN/m between water and a compound (Dow Fluid 200), similar to the present silicone oil. This value represents a difference of 16–19 mN/m between the interfacial tensions of the two oils with water; a divergence sufficient to

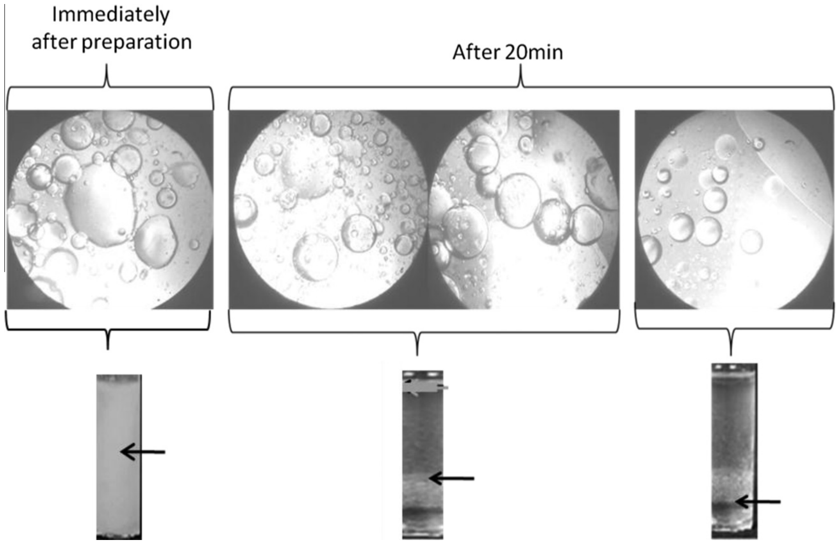

Figure 5 Microscopy photographs of the emulsion after different times (above) and locations as marked on the test tubes beneath the photographs. Magnification 10 × 10.

ensure spreading of the vegetable oil onto water in a three-compound encounter, since the interfacial tension between the oils is at one level of magnitude lower (Rashnidia et al., 1992; Birikh et al., 2003). These values would indicate the configuration to be double emulsions of actual W drop and a layer of VO between the W and the SO continuous phase. However, no drops of that kind were found experimentally and an analysis of the interfacial tension relationship is essential to understand the results. This analysis is made by first relating the interfacial tensions and the contact angles at a line W/VO/SO (Fig. 6).

Equilibrium at the intersection gives

$$\gamma_{SO/W} = \gamma_{SO/VO}\cos\alpha + \gamma_{W/VO}\cos\beta \quad (1)$$

$$\gamma_{SO/VO} = \gamma_{SO/W}\cos\alpha + \gamma_{W/VO}\cos\delta \quad (2)$$

$$\gamma_{W/VO} = \gamma_{W/SO}\cos\beta + \gamma_{VO/SO}\cos\delta \quad (3)$$

and solving for the cosines of α, β, and δ as function of $\gamma_{SO/W}$, $\gamma_{SO/VO}$, and $\gamma_{W/VO}$

$$\cos\alpha = 1/2[(\gamma_{W/SO}/\gamma_{SO/VO}) + (\gamma_{SO/VO}/\gamma_{W/SO}) - (\gamma^2_{W/VO}/\gamma_{W/SO}\gamma_{SO/VO})] \quad (4)$$

$$\cos\beta = 1/2[(\gamma_{W/SO}/\gamma_{W/VO}) + (\gamma_{W/VO}/\gamma_{W/SO}) - (\gamma^2_{SO/VO}/\gamma_{W/VO}\gamma_{W/SO})] \quad (5)$$

$$\cos\delta = 1/2[(\gamma_{W/VO}/\gamma_{VO/SO}) + (\gamma_{W/SO}/\gamma_{W/VO}) - (\gamma^2_{W/SO}/\gamma_{W/VO}\gamma_{SO/VO})] \quad (6)$$

Solving shows, as expected, numerical values outside the limits of the cosines, confirming the spreading of VO. However, such a calculation is concerned with equilibrium on a flat surface and in an emulsion the geometry of the drops and the resultant difference in interfacial energies may also be factor, albeit indirectly and an evaluation of these may be useful. The model for such an investigation consists of central drops, I Fig. 7, with a radius of unity, covered by middle layer, M, of dimension, d_M, or separate drops in the continuous phase, C. Although emulsion formation is a kinetic process and equilibrium with equilibrium conditions is only of secondary importance, the difference in surface free energy between these configurations is of interest.

In the latter case the radius of the drop I is still unity, while the radius of drop M becomes $r_M = [(1 + d_M)^3 - 1]^{1/3}$.

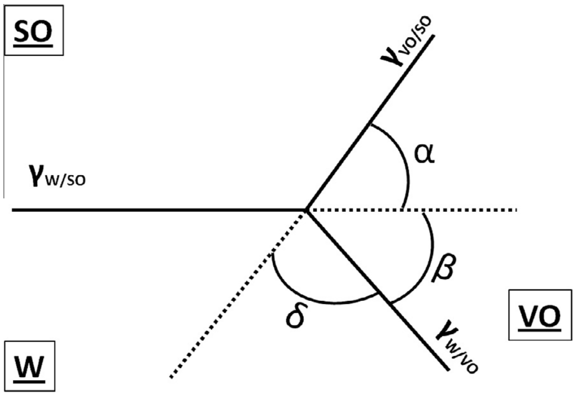

Figure 6 The interfacial tensions and angles for the intersection between the three liquids. W, water; VO, vegetable oil; SO, silicone oil.

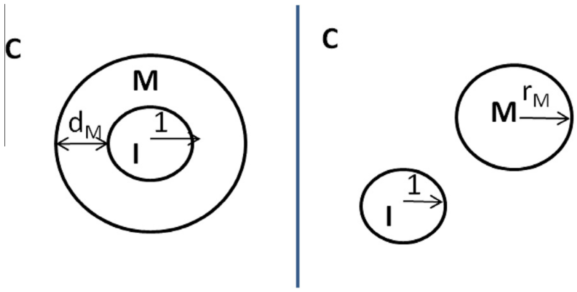

Figure 7 Model drops in an emulsion continuous in compound **C**. To the left the central drop I is surrounded by a layer of compound **M**, while to the right the drops exist individually.

Volumes and areas are: the volume of the central water drop is $4\pi/3$ and its area 4π. Adding a layer of M with dimension d_M gives a total volume of $4\pi(1 + d_M)^3/3$ and an outer area of $4\pi(1 + d_M)^2$ and a volume of the M layer of $4\pi[(1 + d_M)^3 - 1]/3$. The two separate drops give an identical area of the I drop and $4\pi[(1 + d_M)^3 - 1]^{2/3}$ to the M drop. Hence, the condition for separate I and M drops to be favored in comparison with a combination drop is that their combined surface free energy, A, is less than that of the I drops covered by the M layer.

Surface free energy of combination drops,

$$4\pi(\gamma_{I/M} + \delta_{M/C}(1+d_M)^2) \tag{7}$$

and of the separate drops;

$$4\pi(\gamma_{I/c} + \gamma_{M/C}(1+d_M)^3 - 1)^{2/3} \tag{8}$$

Prior to evaluating the relative size of the terms, it is useful to examine the two extreme cases of $d_M = 0$ and $d_M \to \infty$. The first case is an emulsion of I/C and the problem of configuration effects become immaterial. In the second case the contribution from the I drop is neglected, since $\mathrm{Lim}[\gamma_{M/C}((1+d_M)^3-1)^{2/3}_{(d_M\to\infty)})$ and $\gamma_{M/C}\,(1 + d_M)^2$ are both $\approx \gamma_{M/C}d_M^2$ and hence $\gg \gamma_{I/c}$ and of $\gamma_{I/M}$. Furthermore, since $\mathrm{Lim}((1+d_M)^3-1)^{2/3}/(1+d_M)^2)_{(d_M\to\infty)} = 1$ the energy evaluations for this case are not only abstruse, but irrelevant for the examination of the experimental results.

The experimental results revealed three groups of emulsions; continuous in one of the three compounds. The experimental evidence, Fig. 3, shows three emulsions continuous in VO, SO and W located from the top down in the test tube. As a consequence, the free energy estimations focuses on the four possible configurations, of which two have combination drops I/M/C or M/I/C, and one case covers the separate drops (M + I)/C. However, the interfacial free energies $\gamma_{M/C}(1 + d_M)^3 - 1)^{2/3})$ and $\gamma_{M/C}(1 + d_M)^2$ both strongly depend on the d_M and a preliminary evaluation of this factor is the first item to be resolved.

A complete evaluation of this factor is rather complex due to the decisive effect of the relative magnitude of the γ:*s* on the results and is not included in this study. Instead, the analysis is simplified by realizing that the M surface contribution to the total interface free energy in both configuration options is a multiple of γ_M only. Furthermore, the geometrical factors relate as $(1+d_M)^3-1)^{2/3} \ll (1+d_M)^2$ for small values of d_M, while increasing fast with the M layer thickness, Fig. 8.

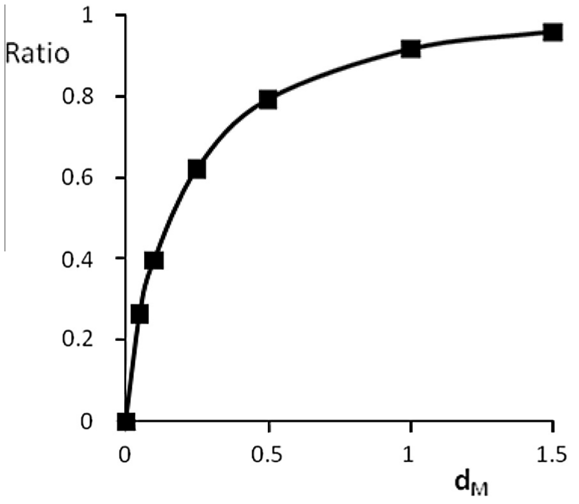

Figure 8 The ratio $(1 + d_M)^3 - 1)^{2/3}/(1 + d_M)^2$ versus d_M expressed as fractions of the central drop radius.

The figure demonstrates the fact that $(1 + d_M)^3 - 1)^{2/3}$ is very much of the same magnitude as $(1 + d_M)^2$ already for the thickness of the M layer reaching a dimension of one half the radius of the central drop. Based on this result, three dimensions of the M layer were chosen. The condition of $d_M < r_I$ is represented by 0.1 times the central drop radius, while $d_M = 0.26$ was selected, because the volume of the M separate drop now is equal to the volume of the central drop and, finally, $d_M = 1.2$ was chosen to illustrate a case of $V_M > 1$. The interfacial free energies from Eqs. (7) and (8) are given in Table 4 and the number for the lowest interfacial energy in bold and underlined.

The numbers in Table 4 provide constructive information about the preferred configurations, with interfacial free energies as the decisive element. The variation in the SO continuous emulsions is the factor of interest, because a cursory evaluation would indicate W to be the central drop, since VO would spread on W. However, the geometrical factor now becomes significant and for small intermediate layer dimensions the VO becomes the central drop and W the intermediate layer. The reason for this counterintuitive result is that the interfacial free energy of a W/SO drop becomes sufficiently small for a radius of certain dimension. For greater dimensions of the intermediate layer the outcome is the expected; the W drop is the central one and the combination drops have a lower energy. It is of some interest to find the dimension of the intermediate layer, when the configuration shifts to water as the inner drop. For that purpose d_M was plotted against the function

$$F = 42((1+d_M)^3-1)^{2/3} - 23.3 - 1.2(1+d_M)^2 \tag{9}$$

Giving an empirical function

$$\mathrm{EF} = 3\times10^{-5}d_M^2 + 0.0073d_M + 0.1331(R^2 = 1.00) \tag{10}$$

The shift from the VO as the central drop in a separate drop configuration to water as the central drop in a combination configuration happens, when the dimension of the intermediate layer exceeds 0.1331 of the radius of the central drop. The remaining cases are also of interest, but not as central and the analysis is neglected. Since only separate drops were observed it must be concluded that the relative free surface energies are a subordinate factor in the emulsion formation.The numbers in Table 4 also has a bearing on which compound formed the continuous phase; especially the fact that of the initial emulsions were predominantly SO continuous, in spite of the fact that the SO volume fraction was only 0.21. According to Table 4 emulsions with a thin intermediate layer showed less interfacial free energies for separate drops. Even so the volume ratios are not excessive; counting also the dispersed W the volume ratio between dispersed and continuous phases is 73/27; a high but not extreme number (Sajjadi et al., 2002; Sajjadi, 2006; Tyrode et al., 2005)The second item of interest is the stability of these emulsions. In general oil/water dispersions without added stabilizer are inherently unstable, because there is no repellant barrier and

Table 4 Interfacial free energies. The combination of lowest combined interfacial free energy is marked by underlined bold font.

Emulsion	d_M			0.1		0.26		1.2	
	γ_{IC}	γ_{IM}	γ_{MC}	Sep.	Comb.	Sep.	Comb.	Sep.	Comb.
W/SO/VO	24.5	42	1.2	25.1	43.5	<u>**25.7**</u>	43.9	<u>**35.0**</u>	52.8
SO/W/VO	1.2	42	24.5	<u>**12.9**</u>	71.6	25.7	80.9	216.2	262.5
W/VO/SO	42	24.5	1.2	42.6	26.0	43.2	<u>**26.4**</u>	52.5	<u>**35.3**</u>
VO/W/SO	1.2	24.5	42	<u>**21.3**</u>	75.3	43.2	91.2	369.8	402.5
VO/SO/W	24.5	1.2	42	44.6	52.0	66.5	67.9	393.1	379.2
SO/VO/W	42	1.2	24.5	53.7	<u>**30.8**</u>	66.5	<u>**40.1**</u>	257.0	<u>**221.7**</u>

the rapid flocculation is immediately followed by coalescence. Since the rate of the latter is huge, large drops are rapidly formed leading to creaming/sedimentation and phase separation promptly occurs. In practice emulsions are stabilized by, "surfactants", amphiphilic medium chain length compounds adsorbing at the interface, but the literature is also rich on alternative stabilizers, such as non-polar polymers (Kamogawa et al., 2003) and solid particles(Midmore, 1998; Binks, 2002; Nonomura et al., 2002; Vignati et al., 2003; Horozov and Binks, 2006; Whitby et al., 2006; Amalvy et al., 2003; Dinsmore et al., 2002) forming surfactant free emulsions (Toshio, 2008). The present emulsions lack any of these stabilizers, i.e., the combination of coalescence with creaming/sedimentation becomes the vital factors to comprehend the results. The latter combination is of special interest, since the densities of the compounds (ρ_{SO} = 0.980 g/cm^3, ρ_{VO} = 0.893 g/cm^3, ρ_W = 0.995 g/cm^3) mean simultaneous rising of the VO drops and sedimentation of the W drops. It would be appealing to calculate the tendency of O/W flocculated drops to gravitate, but very few of these were observed, Fig. 5, and the vertical velocity may be estimated from the Stokes law for a dilute system; $v = \Delta\rho g r^2/9\eta$. Since the density difference between the two oils is six times greater than between SO and W and the VO drops in the SO emulsion appear larger than the water drops, Fig. 5, the equation logically and expectedly predicts the faster formation of the VO emulsion, Fig. 4.

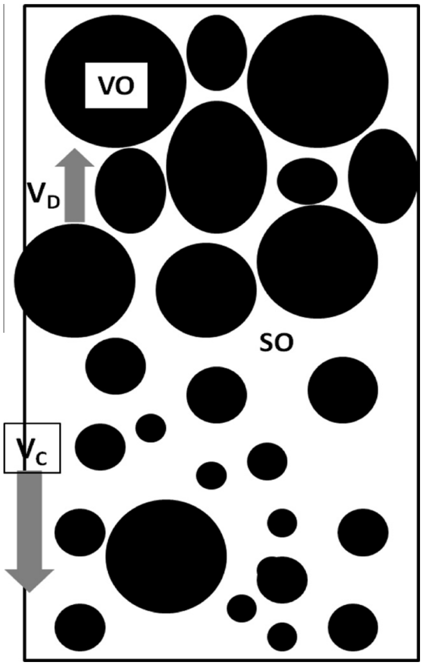

Figure 9 Schematic representation of the two flows in the creaming process of a moderately high internal volume ratio emulsion.

As mentioned earlier, the separation process of the VO cannot be treated with the traditional approach of calculating the rising velocity of the drops by balancing the buoyancy and frictional forces, because the emulsion has a high internal volume ratio; making the flow conditions more complex. Fig. 9 makes it obvious that the rate-determining factor of the VO drops to reach the surface of the SO emulsion is the downward flow of the SO in the constricted space between the VO drops.

Finally the fact needs an explanation that a layer of SO remained on top in the emulsion in spite of the fact that the density difference between SO and VO is significant, 87 kg/m^3. An investigation demonstrated the arrangement to withstand a significant weight of the SO drop, before falling to the bottom of the vessel (see Fig. 10).

A calculation of the maximum drop weight assuming the interfacial tension between VO and SO equals 1.2 mN/m and that the VO preferentially wets the glass surface shows the surface tension force as the anti-gravitational force equals 2.4 10^{-4} N. A half sphere filling the top part would exert a gravitation force of approximately 7.5 10^{-3} N and would certainly fall through the SO layer. Since the gravitational force increases by an exponent of three while the surface tension force only by one it is instructive to calculate the radius of the test tube that would balance the two forces.

$$2\pi r\gamma_{VO/SO} = 87.2\pi r^3/3 \tag{11}$$

$$r = ((3.6\cdot 10^{-3})/87)^{1/2} = 6.4\cdot 10^{-3}\mathrm{m} \tag{12}$$

The actual dimension of the test tube was 0.011 m, and the fact that sufficiently large drops could break through the SO layer is confirmed.

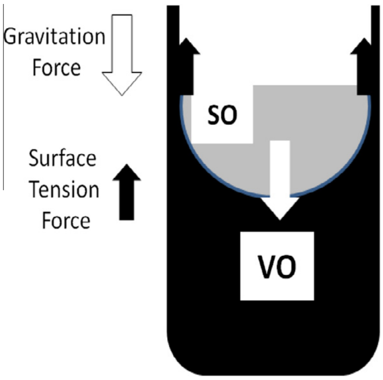

Figure 10 The forces on a sphere at the VO/SO interface.

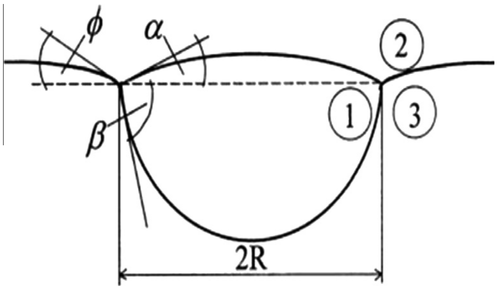

Figure 11 The schematic view of liquid matte lens (1) at the slag (3)/gas(2) interface (Kaptay, 2001).

An exact solution to the problem of the passage of a drop through an interface due to gravitational forces was given by Kaptay (2001) (Fig. 11). Kaptay determined the maximum drop size of a Cu_2S–FeS, matte, floating on liquid low iron wollastonite slag in the copper matte smelting process. With the interfacial tensions and the contact angles in Fig. 11 (Kaptay, 2001) known, the critical drop size was given as

$$R_{cr} = [(2 \cdot \gamma_{1/3} \cdot (1 + \cos\beta)/(g \cdot (\rho_1 - \rho_3))]^{1/2} \qquad (13)$$

The necessary information to apply Eq. (13) is at present not available; sufficiently accurate measurements of the involved factors are in progress.

5. Conclusion

The destabilization process in three-phase emulsions of water, a vegetable oil and strongly hydrophobic silicone oil was investigated. The emulsions were highly unstable with no mutual solubility between the three liquids and with the absence of surfactant. The results showed the presence of water made the emulsions less stable and in addition resulted in a difference in the initial emulsion. The investigation focused on a combination of coalescence and sedimentation/creaming processes. With no water present, the system was only of the type VO/SO single emulsion, while with water present two types of emulsions were formed.

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