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PAPER

Heteroaggregation of water-in-oil droplets: the effects of relative internal solute concentrations and size†

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An attractive interaction between disparately-sized aqueous droplets dispersed in oil has been observed: small salty water droplets tend to stick to and withdraw water from larger droplets that have the same or lower salinity (if <100 mM). The attractive interaction, however, is not observed if small droplets are mixed with droplets that are both larger and saltier. In the latter case, provided there is insufficient salt present in the small droplets to prevent it, the larger droplets grow by a compositional ripening mechanism.

1 Introduction

Emulsions are dispersions of one or more liquid phases in another immiscible liquid. They have widespread industrial and academic use.

The stability of dispersions against aggregation can be described by DLVO theory.[1,2] This theory considers the contributions of van der Waals and electrostatic interactions to a total governing interaction potential as a function of particle separation. Maxima in the potential, due to repulsive electrostatic effects or provision of surfactant, can impart stability if they are of sufficient magnitude relative to the thermal kinetic energy of the dispersion's particles. Minima are established in regions where attractive van der Waals potentials dominate. Extensions to DLVO theory for soft materials include effects of deformation that can provide an elastic repulsive potential.[3]

In addition to aggregation, emulsions undergo additional destabilizing mechanisms as a consequence of redistribution of the droplet phase. This process is known as coarsening, and may proceed *via* several processes: notably coalescence and Ostwald ripening.[4]

Coalescence is the fusion of two or more droplets upon contact; these effects may be reduced or stopped through addition of a stabilizing agent, namely a surfactant.

Ostwald ripening is a process whereby the droplet phase diffuses between droplets as a consequence of chemical potential gradients. Droplets are subject to the Laplace pressure, which is proportional to interfacial tension and inversely proportional to size. Small droplets experience a higher Laplace pressure and, hence, exhibit a higher chemical potential than their larger counterparts. The gradual dissolution of small droplets and subsequent growth of larger droplets reduces the overall Gibbs energy of the system.

Inter-droplet diffusion may be influenced through control of the solubility of the core phase in the continuous phase. The diffusive rate may be slowed or stopped altogether if a component that is insoluble in the continuous phase is dissolved in the dispersed phase.[5] In the case of oil-in-water (O/W) emulsions, the insoluble component may be a large alkane such as hexadecane, while salt may play an analogous role in inverse W/O emulsions. Varying the nature of the intervening medium, such as varying its polarity, also has a similar effect.[6] An additional ripening mechanism, known as compositional ripening, is evident in cases of mixed emulsions whose droplets contain differing concentrations of insoluble components.[7] In such cases the direction of mass transfer between droplet species can be dominated by the droplets' relative chemical potential rather than their respective Laplace pressures.[8]

It has been established that the presence of salt in concentrated W/O emulsions generally stabilizes them against coarsening[9] and, additionally, imparts stability during freeze-thaw cycles.[10] It was postulated that the presence of ions at the water–oil interface may promote surfactant adsorption, even in the case of non-ionics, and thereby enhance stability. Attempts to freeze-thaw high volume fraction pure water-in-oil emulsions failed, and yielded an O/W dispersion in the frozen state. In contrast, when salt was present, a liquid electrolyte-rich fraction formed at the O/W interface upon freezing that maintained stability.[10] While the presence of $MgSO_4$ in aqueous droplet phases has been observed to impart stability to coalescence, the tendency of droplets to flocculate upon standing may increase.[11] The presence of salt has a kinetic impact upon non-ionic surfactant adsorption at W/O interfaces, due to decreased hydration of the polar head group, and equilibrium interfacial tensions are often not achieved during emulsification.[12] Increasing internal salt concentrations therefore tend to increase emulsion droplet sizes;[13] hence the resultant increase in droplet weight overcomes repulsive

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droplet interactions in their sedimented state leading to flocculation.[11]

The stability of NaCl solution dispersions in mineral oil were investigated by Koroleva.[14] Results were interpreted in terms of the difference between osmotic and Laplace pressures established by droplet size and ionic strength. Theoretical consideration of these parameters suggested a critical sodium chloride concentration of 0.012 M, below which Ostwald ripening progressed to the extent that small droplets dissolved completely, while at higher concentrations the droplet number density remained constant. Ostwald ripening was considered to be arrested completely if the initial NaCl concentration in the droplet exceeded 0.188 M.

The presence of salt in mixed emulsions may also have a destabilizing effect. The stability of mixtures of 100 nm water-in-oil and brine-in-oil emulsions has been investigated using binary dye species, isotopic labelling and light scattering.[15] The individual emulsions were stable, but rapid coalescence was indicated upon their combination. It was hypothesized that diffusive water transfer may have formed the basis of a film rupture mechanism.

Recent work has investigated controlled aggregation of O/W emulsions using pH-sensitive surfactants to regulate charge stabilization.[16]

In the work presented here we consider the stability of mixed emulsions of differently sized W/O droplets that also differ in their relative salinities, and describe an interaction that depends upon these parameters. Both types of particles are stabilized by the same non-ionic surfactant.

2 Experimental

n-Dodecane (99%, Aldrich), BP2629-1 mineral oil (Fisher), KCl (99%, Aldrich) and Sorbitan monooleate (Span 80, Fluka) were used as received. Ultra-pure deionized water (resistivity 18 MΩ cm) was sourced from an Elga Purelab Ultra.

Large W/O droplets with a narrow size distribution were prepared using a polydimethylsiloxane microfluidic cell. The cell had been formed using a Dow Corning SYLGARD 184 elastomer kit and a silicon wafer-mounted etched photoresist master template; and was fused onto a glass microscope slide as described elsewhere.[16,17] The cell comprised an inlet for oil to a bifurcating channel, the ends of which joined with a water inlet channel at a droplet generating junction[18] that continued to an outlet for droplet collection. 75 and 100 μm width channels were used. Deionized water, 1, 10, and 100 mM KCl solutions were used as internal phases. The emulsions were formed from 1 : 2 volume ratios of aqueous solution and 1 wt. % Span 80 in mineral oil (the cell was incompatible with dodecane); and these separate phases were injected into their respective inlets with flow rates of 0.8 and 1.5 μl min^{-1}.

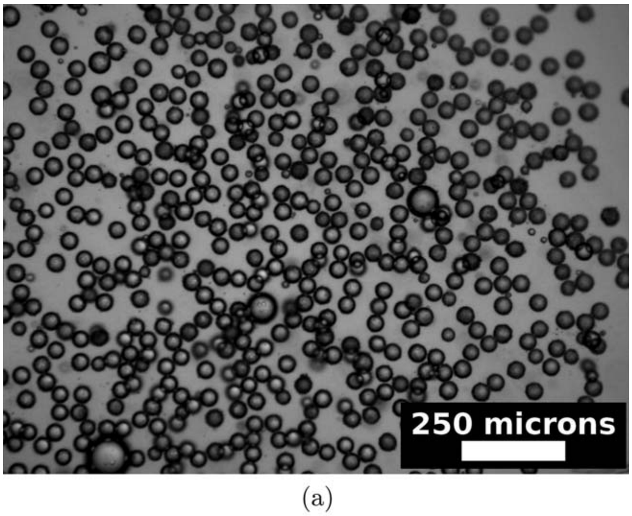
Smaller, polydispersed, emulsions were prepared using a Silverson SL2 mixer. Pure water, or KCl solutions ranging from 1 mM to 1 M, were added *via* a syringe pump at a rate of 1 ml min^{-1} to a sheared mixture of 0.3 wt.% Span 80 in dodecane to yield a final emulsion volume fraction of 0.005.

Microscopy studies were undertaken with a Leica DME microscope fitted with a digital camera. Typically a single droplet (approx. 10 μL) of large-droplet emulsion was added to 1 ml of the polydisperse emulsion, with gentle agitation, and the mixture was transferred to a slide-mounted chamber and topped with a coverslip to prevent droplet evaporation. Images were recorded onto a PC, *via* a capture card, periodically over 3 h.

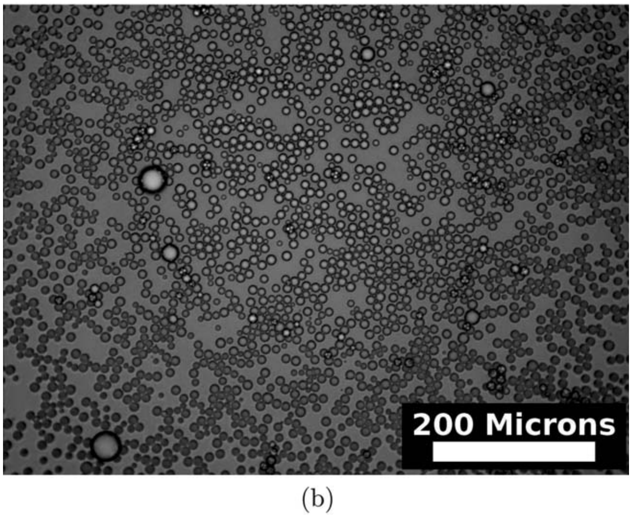
3 Results and discussion

The microfluidic cell-derived emulsions tended to be of narrow size distribution, typically with mean diameters in the range of 10–50 μm with standard deviations in size less than 20%. Fig. 1(a) and 1(b) are micrographs of pure water and 100 mM emulsions respectively. The emulsions sedimented due to their large size, but were stable to coalescence in that state over a period of three months.

Combination of large and small emulsions presented two disparate behaviours. If the smaller droplets were of a lower salt concentration than the larger microfluidic ones (Fig. 2(a)), or



(a)



(b)

Fig. 1 (a) A representative deionized water-in-mineral oil emulsion produced from the microfluidic channel. The mean diameter, estimated from micrograph chord measurements, was 40.7 μm with a standard deviation of 16% ($n = 314$). (b) A 100 mM KCl microfluidic emulsion. The estimated mean diameter was 9.8 μm with a standard deviation of 17% ($n = 357$).

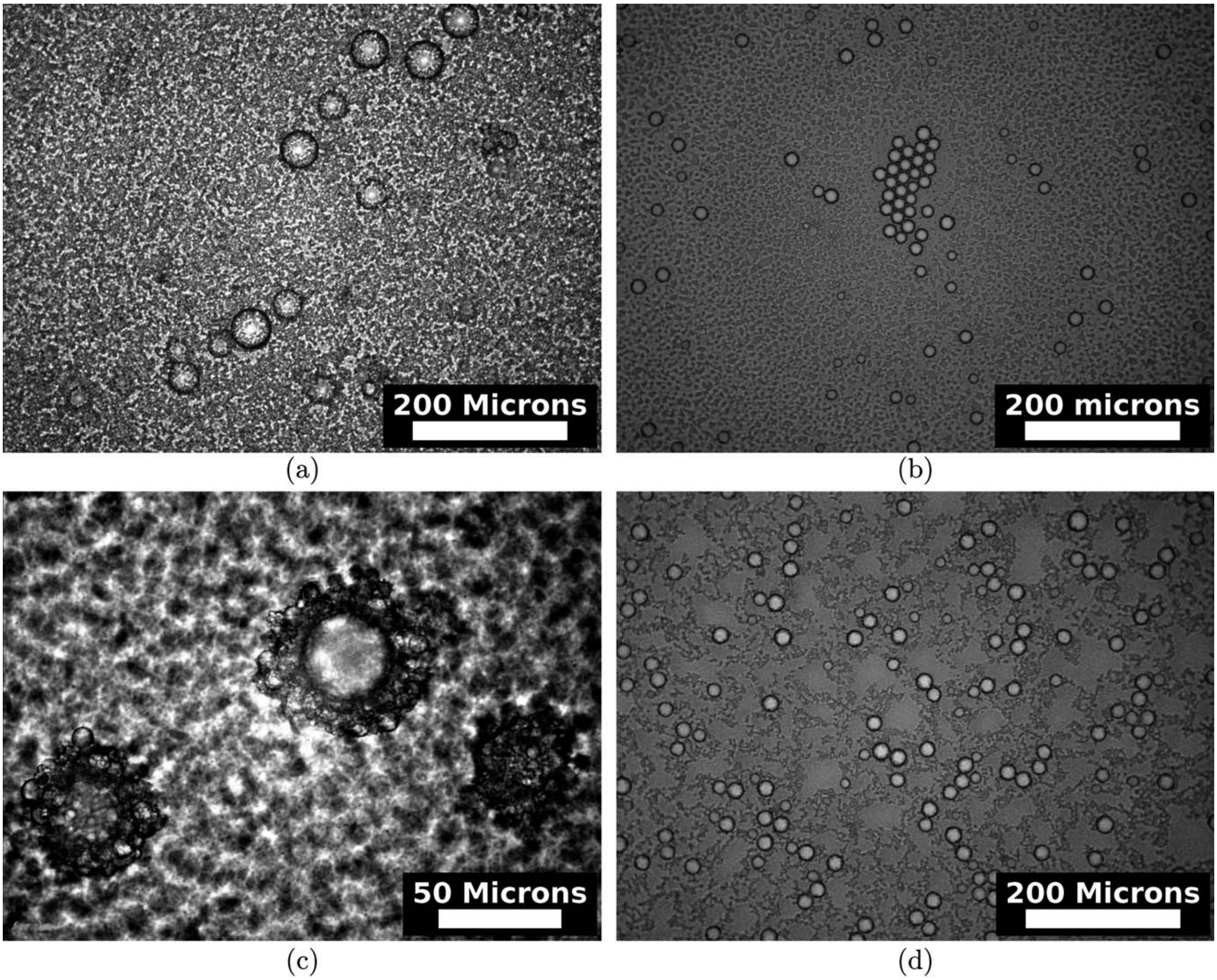


Fig. 2 (a) Large 10 mM KCl droplets with a smaller 1 mM KCl emulsion, 2 h 15 min after initial combination. (b) Large 100 mM droplets with smaller pure water droplets 3 h after mixing. Rather than sticking to the larger saline droplets, the water droplets settle onto the microscope slide surface with apparent wetting. (c) Large pure water droplets combined with smaller 100 mM KCl droplets 80 min after combination. The encapsulating droplets consume the cores. (d) Large 100 mM droplets with small 1 M KCl droplets, 4 h after combination. Osmotic pressure established within the larger droplets limits water diffusion from them towards the smaller, saltier droplets nearby.

contained no salt (Fig. 2(b)), the droplets remained distinct. Small droplet aggregation with larger droplets was observed, however, if the small droplets were possessed of an equivalent or higher internal salt concentration (Fig. 2(c)). Droplet aggregation occurred rapidly and was evident immediately upon commencement of microscope study (approximately 1–2 min after the initial combination). The exceptions to this general trend were systems involving large 100 mM droplets. In those cases no droplet aggregation was observed irrespective of the small droplet concentrations tested (up to 1 M: Fig. 2(d)). Further micrographs of aggregation of small 1 mM KCl droplets with large pure water droplets, and small 1 M KCl droplets with large 10 mM KCl droplets are available in the supplementary material.

The large microfluidic droplets, upon combination with smaller droplets, changed size (Table 1). In the non-aggregating cases the large droplets tended to grow (Fig. 3(a)). In the aggregated cases the core droplets shrank with time because their content passed into encapsulating droplets (Fig. 3(b)). The relative reduction in size of the core volumes over a 2-hour period were similar if the droplets contained different salt concentrations. In the case of aggregates whose droplets were of equivalent

Table 1 The mean percentage change in large droplet diameter, d, after 2 h for mixtures of large droplets and small droplets comprising internal KCl concentrations of c_L and c_s respectively

c_L/mM	c_s/mM	Δd/%	State
0	1.0	-19 ± 3	Aggregated
10	1.0	$+5 \pm 4$	Non-aggregated
10	10	-5 ± 3	Aggregated
10	100	-22 ± 6	Aggregated
100	0	$+45 \pm 3$	Non-aggregated
0	100	-19 ± 3	Non-aggregated[a]

[a] After 1 h.

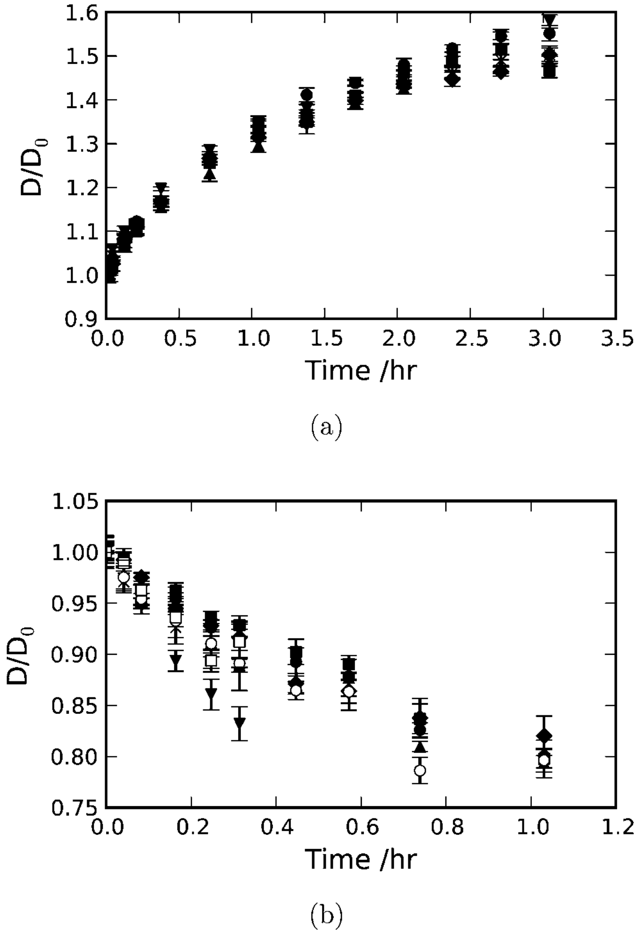


Fig. 3 (a) The growth of large 100 mM droplets, in proximity to smaller pure water droplets, scaled by their initial size. Six individual droplets were measured. (b) Aggregate pure water core diameters scaled by their initial size. The cores shrink as water is transferred to the encapsulating smaller 100 mM droplets. A focal plane was selected that allowed reasonable estimation of the core diameter. Eight individual droplets were measured with time.

internal salt concentration, the core droplet diameter reduction was significantly less, presumably as a consequence of a smaller chemical potential gradient.

The differences in stability to aggregation seem to correlate with the direction of mass transfer between the droplets. Where smaller droplets transfer water to their larger counterparts, presumably through an Ostwald ripening mechanism, no aggregation is observed. Aggregation is observed when water transfers from large droplets to smaller ones.

The presence of higher salt concentrations in the smaller droplets may reverse the chemical potential gradients that drive Ostwald ripening. Water transfer by diffusion from large droplets to nearby smaller ones will cause the latter to grow. The changes in relative size then have implications for the droplets' attractive inter-droplet van der Waals potential (W_{vdw}). This potential may be calculated for two differently sized droplets of radii a_1 and a_2 with centre-to-centre separation r using eqn (1).[19] The parameter A in eqn (1) is the Hamaker constant.

$$W_{vdw} = -\frac{A}{6}\left(\frac{2a_1a_2}{r^2-(a_1+a_2)^2} + \frac{2a_1a_2}{r^2-(a_1-a_2)^2} + \ln\frac{r^2-(a_1+a_2)^2}{r^2-(a_1-a_2)^2}\right) \quad (1)$$

Fig. 4(a) plots W_{vdw} for an initial condition of a droplet of radius 10 μm in proximity to a droplet with a 1 μm radius. A value of 0.5 × 10^{-20} was used as the Hamaker constant for a water–dodecane–water interaction;[20] this is valid because oil–water–oil and water–oil–water Hamaker constants are comparable.[21] The changes in the potential profiles are also plotted for a case in which 80% of the smaller droplet volume is transferred to the large droplet, and an opposite extreme case in which volume transfer from the large droplet continued until the two droplets were of equivalent size. Upon transfer of volume from the small droplet to the large droplet there is a corresponding reduction in the magnitude of the van der Waals potential for small separations and the extent of this potential is reduced. In the opposite case, volume transfer from the large droplet leads

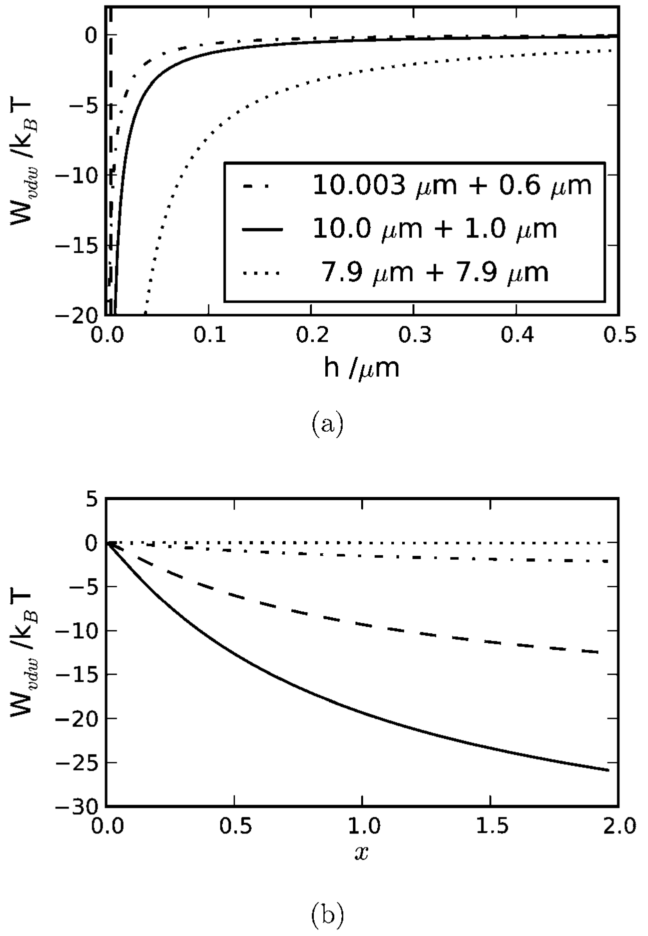


Fig. 4 (a) The van der Waals potential as a function of surface-to-surface separation, h for two droplets. The dashed line represents the extent of surface-adsorbed surfactant. (b) The van der Waals potential scaled by k_BT at a surface-to-surface separation of 5 nm as a function of x for different droplet radii: 10 nm (dotted), 100 nm (dash-dotted), 500 nm (dashes) and 1000 nm (solid line).

both to an increase in the magnitude and extent of the van der Waals potential.

A diffusive mechanism for these effects is therefore proposed. Water transfer by conventional Ostwald ripening reduces the small droplet size and hence the magnitude and extent of the van der Waals potential it experiences. Repulsive surfactant interactions and thermal energy then prove sufficient to prevent droplet aggregation. In the alternative case, transfer of water from large droplets to small droplets across an intervening media causes the smaller droplet to grow and increases the depth of the intervening van der Waals potential. The droplets are drawn closer together, which increases volume transfer efficiency thereby causing the small droplet to grow to such an extent that a van der Waals potential of sufficient depth extends beyond the influence of stabilizing surfactant: the droplets stick together. As the heteroaggregate grows, nearby small droplets will experience a corresponding increase in van der Waals potential.

No heteroaggregation was observed when the internal KCl concentration of the large droplets was 100 mM and the small droplets were 1 M (Fig. 2(d)). In that case, the salt concentration in the large droplets may be sufficient to reduce or prevent their volume transfer. There was no evidence of enhanced droplet number density in vicinity to the larger droplets. The large droplets were observed to grow in size, however, possibly as a result of surfactant mediated transfer or coalescence.[15] It is also worth noting that salt concentrations >1 M have previously been reported to reduce the elastic behaviour of Span80 films to the detriment of their stability.[12]

The fate of small, less saline droplets in proximity to larger and saltier counterparts is not clear from this study. While it was possible to follow multi-micrometre-sized droplets *via* microscopy, small sub-micron droplets could not be resolved. Droplet coalescence should not be discounted therefore. Droplets of several micrometres in diameter were, however, observed to drift into apparent contact with the larger microfluidic cell-derived droplets and then drift away again under Brownian motion. It is worth noting that droplet coalescence between the smaller droplets and the core large droplets in the heteroaggregating systems manifestly did not occur over the timescales the emulsions were inspected by microscopy. The droplet-adsorbed surfactant concentrations were sufficient to prevent coalescence in these cases. Film thinning and coalescence would be expected should surfactant be inducted away from the shrinking large droplet to the surrounding layers of growing smaller droplets. Further study investigating the influence of surfactant concentration on the formation and stability of the aggregated structures would therefore be of interest.

The magnitude of the van der Waals potential is sensitive to the droplets' respective sizes. A scaling factor x may be introduced into a surface-to-surface form of eqn (1) to replace the droplet radius a_2 ($x = a_2/a_1$). Fig. 4(b) plots the van der Waals potential at a fixed surface-to-surface separation of 5 nm as a function of the droplet radius scaling term x for sub-micron and multi-micron-sized droplets. This separation lies beyond the extent of the stabilizing steric effects of the surfactant, though, as noted above, other repulsive interactions may be present. The analysis suggests that core droplets approaching micron size will establish a significant potential well for droplets half their size. We note a study of solid heteroaggregating systems by Furusawa and Anzai shows that a relative particle size ratio greater than 3 is required for core-shell-type aggregates to form, while larger aggregate masses form at lower ratios.[22]

4 Conclusions

In summary, we report aggregation events in mixtures of disparately-sized W/O emulsions subject to relative internal salt concentration. Provided smaller droplets do not have a lower salt concentrations than their larger counterparts, the droplets aggregate to give a core-shell structure. The core droplet size decreases as its content transfers to the engulfing droplets. The aggregation is not observed if the larger droplets contain a higher salt concentration than nearby smaller droplets.

Consideration of the van der Waals interaction potential between differently sized droplets suggests that upon increase of nearby small droplet size there is an extension of the range of this attractive potential, and an increase in its well depth. This effect is established if diffusive transfer of water from large droplets to nearby smaller ones occurs. The aggregation is generally destabilizing, since the aggregate continues to attract nearby droplets.

In the counter cases, in which the large droplet comprises the higher salt concentration, water diffuses from the small droplets *via* compositional ripening and reduces the magnitude of the inter-droplet van der Waals potential.

This aggregation mechanism may find use as the basis for formation of core-shell particles if the smaller droplets act as a conduit for shell-forming components. It may prove useful for microfluidic lab-on-a-chip applications where the immediate environment may be controlled to prevent wholesale aggregation; indeed the van der Waals-based hypothesis suggests the effect is more important for droplets of size regimes typically produced by these methods. Also, large droplets could be used to scavenge smaller solute-rich droplets from dispersions.

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