



Emulsions stabilised solely by colloidal particles

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Abstract

The preparation and properties of emulsions, stabilised solely by the adsorption of solid particles at the oil–water interface, are reviewed especially in the light of our own work with particles of well-controlled surface properties. Where appropriate, comparison is made with the behaviour of surfactant-stabilised emulsions. Hydrophilic particles tend to form oil-in-water (o/w) emulsions whereas hydrophobic particles form water-in-oil (w/o) emulsions. Many of the properties can be attributed to the very large free energy of adsorption for particles of intermediate wettability (contact angle at the oil–water interface, say, between 50 and 130°). This effectively irreversible adsorption leads to extreme stability for certain emulsions and is in contrast to the behaviour of surfactant molecules which are usually in rapid dynamic equilibrium between the oil–water interface and the bulk phases. There is evidence that, in some systems, weak flocculation of the particles improves the emulsion stability. Phase inversion from w/o to o/w can be brought about by increasing the volume fraction of water. Emulsions close to this inversion point tend to be the most stable, again in contrast to surfactant systems. The volume fraction needed for inversion depends on the particle wettability and the nature of the oil and these effects have been rationalised in terms of surface energy components. Stable multiple emulsions (w/o/w and o/w/o) can be made using two types of particles with slightly different wettability. Similar multiple emulsions prepared with two types of surfactant tend to be much less stable. The possibility of preparing novel solid materials by evaporating solid-stabilised emulsions is also proposed. Finally we report on some extensions to the work of Levine et al. who obtained expressions for the free energy of formation of emulsion drops covered with close-packed monolayers of monodis-

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perse spherical particles. In particular in the light of the observations that nanoparticles can act as excellent emulsion stabilisers, we have considered potential effects on the free energy of emulsion formation of the action of small (physically realistic) positive and negative line tensions in the 3-phase contact lines skirting particles adsorbed at the droplet interfaces. We also explore the possibility that curvature properties of close-packed particle monolayers can affect emulsion properties in much the same way that surfactant monolayer properties influence emulsion type and stability.

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1. Introduction

It is now well established that low molar mass surfactants and surface-active polymers are used to aid dispersion of powdered materials in a liquid, can form a variety of aggregated structures in aqueous or non-aqueous media and are frequently employed as emulsifiers in the preparation of emulsions and as stabilisers in the production of foams. Much less well appreciated is that solid particles (nano- or micro-) can function in similar ways to surfactant molecules but certain differences in behaviour are inevitable, e.g. particles do not assemble into aggregates in the same way that surfactant molecules form micelles and hence solubilisation phenomena are absent in the particle case. There has been a resurgence of interest recently in the field of particles at interfaces (both planar and curved), partly as a result of the current activity in nanoparticle technology for producing new materials [1]. A review by one of us [2] has described the recent advances in the areas of particle monolayers at fluid–fluid interfaces, determination of contact angles of small particles, partitioning of particles between phases and solid–stabilised foams, highlighting the similarities and differences between the two types of stabiliser. The present review deals with emulsions, i.e. mixtures of oil and water, stabilised solely by colloidal particles. The ideas originating from investigating simple emulsions are extended to the preparation of multiple emulsions and a brief account is given of the use of such emulsions as templates for the formation of porous solid phases.

We report also on some extensions to the work of Levine et al. who obtained expressions for the free energy of formation of emulsion drops covered with close-packed monolayers of monodisperse spherical particles. In particular we have considered potential effects on the free energy of emulsion formation of the action of line tension in the 3-phase contact lines around particles adsorbed at the droplet interfaces. We also explore the possibility that curvature properties of close-packed particle monolayers can affect emulsion properties in much the same way that surfactant monolayer properties influence emulsion type and stability.

2. Simple emulsions

For surfactant molecules present in oil + water mixtures, the system hydrophile–lipophile balance (HLB) is the important parameter in determining whether aggre-

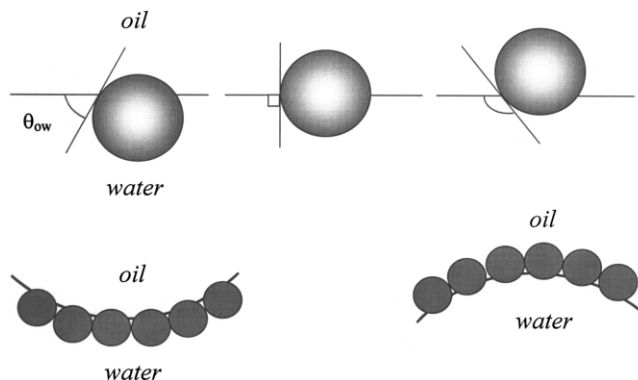


Fig. 1. (upper) Position of a small spherical particle at a planar oil–water interface for a contact angle (measured through the aqueous phase) less than 90° (left), equal to 90° (centre) and greater than 90° (right). (lower) Corresponding probable positioning of particles at a curved interface. For $\theta < 90^\circ$, solid-stabilised o/w emulsions may form (left). For $\theta > 90^\circ$, solid-stabilised w/o emulsions may form (right).

gated surfactant (micelles or microemulsion droplets) resides in either water, oil or a third phase [3]. It has been shown that the packing parameter of the surfactant in situ at the oil–water interface determines the tendency of the surfactant monolayer to curve towards water or oil or remain effectively planar. This in turn is set by the geometry of the surfactant molecules, hydrated by water on one side of the monolayer and solvated by oil on the other. For hydrophilic surfactants (non-ionics with a high degree of ethoxylation or ionics in the absence of salt), the area per head group is larger than that of the chain and monolayers curve around oil resulting in oil-in-water (o/w) micro- and macroemulsions. For more lipophilic surfactants (non-ionics with low degrees of ethoxylation or ionics in the presence of sufficient salt), the area per chain exceeds that of the head group and water becomes the dispersed phase in water-in-oil (w/o) micro- and macroemulsions. In the case of spherical particles, which adsorb to interfaces, the relevant parameter is thought to be the contact angle θ_{ow} which the particle makes with the interface (Fig. 1). For hydrophilic particles, e.g. metal oxides, θ_{ow} measured into the aqueous phase is normally $< 90^\circ$ and a larger fraction of the particle surface resides in water than in oil. For hydrophobic particles, e.g. suitably treated silica, θ_{ow} is generally greater than 90° and the particle resides more in oil than in water. By analogy with surfactant molecules, the monolayers will curve such that the larger area of the particle surface remains on the external side, giving rise to o/w emulsions when $\theta_{ow} < 90^\circ$ and w/o emulsions when $\theta_{ow} > 90^\circ$.

Many methods exist to synthesise small, monodisperse particles of different shape and surface coating. If the coating, e.g. alkylsilane, is homogeneous over the particle surface following reaction in the vapour phase, such particles are surface-active but, unlike surfactants, are not amphiphilic. If, however, the coating can be restricted to a particular area of the surface only, heterogeneous or ‘Janus’ particles result which are both surface-active and amphiphilic, i.e. the particle has a specific area which

is water-liking and a specific area which is oil-liking. Assuming that the particle is small enough (typically less than a micron in diameter) so that the effect of gravity is negligible, the energy ($-\Delta_{\text{int}}G$) required to remove a particle of radius r from an oil-water interface of tension γ_{ow} is given by [4]

$$-\Delta_{\text{int}}G = \pi r^2 \gamma_{\text{ow}} (1 \pm \cos \theta_{\text{ow}})^2 \quad (1)$$

in which the sign inside the bracket is negative for removal into the water phase, and positive for removal into oil. Inspection of Eq. (1) for given $r = 10^{-8}$ m (characteristic of fumed silica, later) and $\gamma_{\text{ow}} = 0.036$ N m $^{-1}$ (toluene–water) shows that the particle is most strongly held in the interface for $\theta_{\text{ow}} = 90^\circ$ with $-\Delta_{\text{int}}G$ being $2750 kT$. Either side of 90° , $-\Delta_{\text{int}}G$ falls rapidly such that for θ_{ow} between 0 and 20° or between 160 and 180° this energy is relatively small ($< 10 kT$). It will be shown later that this extreme variation of $-\Delta_{\text{int}}G$ with particle wettability has a major influence on the ability of particles of different hydrophobicity to stabilise emulsions. For angles $< 90^\circ$ the particle is more easily removed into water than oil, i.e. it is relatively hydrophilic, and for $\theta_{\text{ow}} > 90^\circ$ the reverse is true, i.e. it is relatively hydrophobic. One consequence of the very high energy of attachment of particles to interfaces is that particles once at interfaces can be thought of as effectively irreversibly adsorbed. This is in sharp contrast to surfactant molecules which adsorb and desorb on a relatively fast timescale. Since $-\Delta_{\text{int}}G$ depends on the square of the particle radius, it decreases markedly for smaller and smaller particles, and for very small particles (< 1 nm radius) of the size comparable to most surfactant molecules detachment is easy (several kT) and they thus may not be too effective as stabilisers.

In a theoretical study [5], Binks and Fletcher considered the difference in the adsorption of a spherical particle to an interface between particles possessing a homogeneous surface of uniform wettability and Janus particles. For the latter, calculations were presented which show how the particle amphiphilicity, tuned by variation of either the relative surface areas or the different wettabilities of the two surface regions on the particles, influences the strength of particle attachment. Increasing the amphiphilicity of the particles produces a maximum of a 3-fold increase in surface activity compared with homogeneously coated particles for average contact angles approximately 90° . In addition, it was shown that, unlike particles of homogeneous surface coating, Janus particles remain strongly surface-active for average contact angles approaching 0 or 180° .

Solid particles have been present in emulsion formulations for many years, including those of the food, paint, agrochemical, pharmaceutical and oil industries. Their presence is thought to contribute to enhanced stability by some means. The fact that finely divided solid particles can act as the stabiliser in emulsions was known since the beginning of the last century. The credit is usually given to Pickering [6] (hence the term ‘Pickering emulsions’), who noted that particles which were wetted more by water than by oil acted as emulsifiers for o/w emulsions by residing at the interface. However, in a paper four years earlier and cited by Pickering, Ramsden [7] described the formation of a membrane of solid particles enveloping both air bubbles in water (foams) and oil drops in water, giving rise

sometimes to ‘persistently deformed sharply angular and grotesque shapes of emulsified globules’! It was not until the work of Finkle et al. [8] that the relationship between the type of solid and emulsion type (o/w or w/o) was recognised. They stated that in an emulsion containing solid particles, one of the liquids would probably wet the solid more than the other liquid, with the more poorly wetting liquid becoming the dispersed phase. The importance of the wettability of the particles at the oil–water interface, quantified by the contact angle θ_{ow} that the particle makes with it, was therefore noted. Thus, water-wet particles like silica should stabilise o/w emulsions and oil-wet particles like carbon black should stabilise w/o emulsions. These ideas were given strong support by the experiments of Schulman and Leja [9] using barium sulfate crystals/powders and surfactant, measuring the relevant contact angles and determining the emulsion type and stability. For conditions such that θ_{ow} (measured through the aqueous phase) was slightly $<90^\circ$ particles stabilised o/w emulsions, but for $\theta_{ow} > 90^\circ$ particles were still held at the interface but now stabilised w/o emulsions. However, if the particles were either too hydrophilic (low θ_{ow}) or too hydrophobic (high θ_{ow}) they tended to remain dispersed in either the aqueous or oil phase, respectively, giving rise to very unstable emulsions. The results in Table 1, taken from work in our laboratory [10], substantiate the link between contact angle and preferred emulsion type (equal oil/water ratio) for a range of systems of different solid type and oil polarity. Inorganic materials always form o/w emulsions whereas organic materials like hydrophobic bentonite or polystyrene always form w/o emulsions. The very important class of partially hydrophobic materials (like silica) stabilise o/w emulsions with non-polar oils ($\theta_{ow} < 90^\circ$) and w/o emulsions with more polar oils like esters or alcohols ($\theta_{ow} > 90^\circ$). An explanation why this is so is given later.

It is surprising that, since the early studies mentioned above, little work in this area appeared in the open literature until quite recently. A wide variety of solid particles has been used as stabilisers of either o/w or w/o emulsions including iron oxide, hydroxides, metal sulfates, silica, clays and carbon. The effectiveness of the solid in stabilising emulsions depends, inter alia, on particle size, particle shape, particle concentration, particle wettability and on the interactions between particles. Particle wettability may be altered by adsorption of suitable surfactants, in some cases leading to emulsion phase inversion. Depending on the exact system, there are at least two mechanisms by which colloidal particles stabilise emulsions. In the first, the particles are required to adsorb at the oil–water interface and remain there forming a dense film (monolayer or multilayer) around the dispersed drops impeding coalescence. An example of such a film is seen in Fig. 2 in which $3.2 \mu\text{m}$ diameter monodisperse polystyrene particles stabilise a water-in-cyclohexane emulsion drop [11]. Although there are regions on the drop surface of hexagonally close-packed particles, there are also regions where this ordering is disturbed and small gaps appear between particle arrays. In the second, additional stabilisation arises when the particle–particle interactions are such that a three-dimensional network of particles develops in the continuous phase surrounding the drops. This has been invoked particularly in clay-containing systems in which the oil drops become captured and more or less immobilised in the array of clay platelets in water [12].

Table 1

Link between emulsion type (1:1 oil/water volume ratio) and contact angle at oil–water interface for different solids and a range of oils. Taken from ref. [10]

Solid	Oil	$\theta_{ow}/^\circ$	Emulsion type
Barium sulfate ^b	Dodecane	0	o/w
	Isopropyl myristate	0	o/w
Calcium carbonate ^b	Dodecane	43	o/w
	Isopropyl myristate	39	o/w
Hydrophilic silica ^a	Dodecane	38	o/w
	Cyclohexane	37	o/w
	PDMS 50 cS	81	o/w
	Isopropyl myristate	32	o/w
	Undecanol	38	o/w
Partially hydrophobic silica ^a	Dodecane	83	o/w
	Cyclohexane	87	o/w
	Isopropyl myristate	101	w/o
	Undecanol	110	w/o
Hydrophobic silica ^a	Dodecane	135	w/o
	Cyclohexane	135	w/o
	PDMS 50 cS	172	w/o
	Isopropyl myristate	> 175	w/o
	Undecanol	151	w/o
Bentonite for organic systems ^b	Dodecane	81	w/o
	Isopropyl myristate	96	w/o
Claytone HY ^b (hydrophobic bentonite)	Dodecane	110	w/o
	Isopropyl myristate	141	w/o
Polystyrene ^a	Dodecane	152	w/o
	PDMS 50 cS	175	w/o
Polytetrafluoroethylene ^a (PTFE)	Dodecane	147	w/o
	Isopropyl myristate	175	w/o
	Undecanol	130	w/o

^a Advancing contact angles of water drops under oil (measured through aqueous phase) were determined on planar substrates with oil contacting solid first.

^b Contact angles calculated from surface energy components using the procedure detailed in ref. [25].

The enhanced viscosity of the continuous phase reduces the rate and extent of creaming. Amongst the teams involved in this field, Tambe and Sharma [13], Yan and Masliyah [14], Zhai and Efrima [15], Midmore [16,17] and Lagaly and colleagues [12,18] have made particularly important contributions to the understanding of particle-stabilised emulsions, frequently in the presence of surfactant or polymer. Even millimetre-sized drops, coated by particles, are shown to be extremely stable to coalescence [15]—a situation which has never been realised in the case of surfactant-stabilised emulsions. The potential for exploiting such stability at these length scales is high.

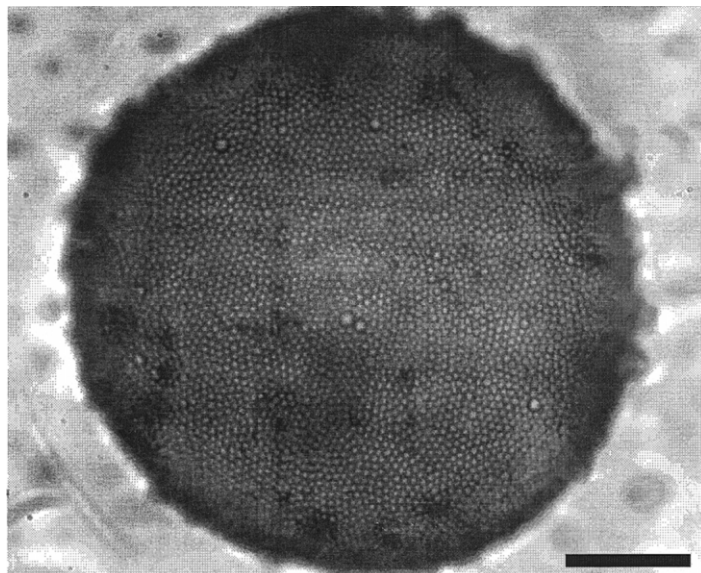


Fig. 2. Optical microscopy image of a water-in-cyclohexane emulsion drop stabilised by monodisperse polystyrene aldehyde/sulfate particles of diameter $3.2\ \mu\text{m}$. The scale bar corresponds to $50\ \mu\text{m}$. Taken from ref. [11].

In a recent series of papers, some unpublished, Binks et al. have systematically investigated the formation, stability and structure of emulsions stabilised entirely by solid particles in an attempt to elucidate unambiguously the role of the particles in such systems [10,11,19–34]. The particle types were silica [19–23], Laponite clay [24] and polystyrene latex [11], and a range of oils was used including alkanes, silicones, alcohols and esters. Such surfactant-free emulsions represent a novel alternative to conventional ones and may prove to be more advantageous too. Simple emulsions of both types are possible but their stability is crucially dependent on the hydrophobicity of the particles. A main objective of part of the work was to investigate and understand the relationship, if any, between the properties of the particle dispersions before emulsification and the ensuing emulsion characteristics. A new method for preparing monodisperse solid-stabilised emulsions has also been described involving the sequential replacement of surfactant by particles at drop interfaces, using dialysis [26]. Such emulsions are more amenable to study and treat using theoretical models than the more common polydisperse ones.

2.1. Effect of particle concentration

For given emulsification conditions, it is of interest to investigate the effect of the initial particle concentration on the average emulsion drop size and stability. Using surfactants, the size typically decreases with concentration until the critical

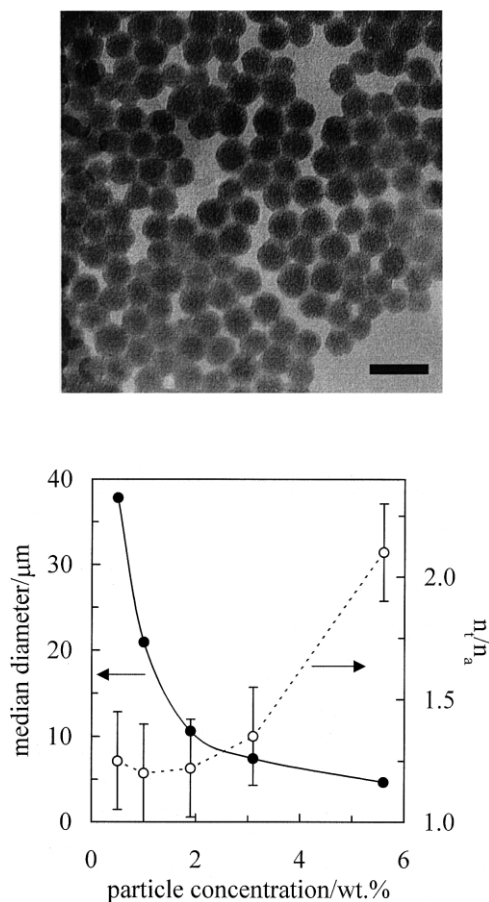


Fig. 3. (upper) Transmission electron microscopy image of monodisperse, spherical, hydrophilic silica particles (ex. Clariant) from an aqueous dispersion. The scale bar corresponds to 50 nm. (lower) Median drop diameter (left hand ordinate, filled points) as a function of aqueous concentration of hydrophobic silica particles (25 nm diameter) in 0.65 cS PDMS-in-water emulsions ($\phi_o=0.33$). Also shown is the ratio of the total number of particles available to the number required to provide a monolayer around all drops (right hand ordinate, open points). Taken from ref. [33].

micelle concentration is reached, whereafter it remains constant. The decrease is mainly as a result of the lowering of the interfacial tension facilitating drop breakup. We have used monodisperse spherical silica particles, 25 nm in diameter, and shown in Fig. 3 (upper) which were subsequently coated with an alkylsilane reagent to render them partially hydrophobic. Emulsions of silicone oil-in-water, $\phi_o=0.33$, were prepared using a high pressure jet homogeniser with particles originally dispersed in water [33]. The median drop diameter immediately after preparation is shown as a function of particle concentration in Fig. 3 (lower) as the filled points. All emulsions were creamy-white in appearance whose viscosity increased with

particle concentration. The size falls by a factor of approximately 8 for a tenfold increase in particle concentration. Assuming that all the particles are adsorbed to form a hexagonally close-packed monolayer, the ratio of the total number of particles (n_t) to the number of particles adsorbed (n_a) can be calculated taking into account the distribution of drop sizes in the emulsions. It can be seen from Fig. 3 (lower, open points) that this ratio is around unity for concentrations up to 3 wt.% and increases to over 2 by 5.6 wt.%, i.e. the drop size is set initially by the particle concentration until a limiting size is reached after which an excess of particles in the continuous phase appears. This excess was confirmed by the presence of a small shoulder of approximately 1 μm in the drop size distribution, due to aggregated silica particles. All emulsions were stable to coalescence but the stability to creaming decreased progressively with decreasing particle concentration in line with the increase in average drop size. An added bonus of using relatively high concentrations of silica particles is that the excess remaining causes gelation of the continuous phase retarding or preventing completely creaming of oil drops or sedimentation of water drops [20]. A product therefore has an extremely long shelf-life and is aesthetically attractive.

2.2. *Effect of electrolyte*

Since the majority of colloidal particles in aqueous dispersions are charged, addition of salt not only reduces their surface potentials but can also lead to coagulation of the particles into flocs. The question we posed was does the initial state of dispersion of the particles in water affect the stability of emulsions formed from them? Earlier work had shown that good emulsion stabilisation was achieved when the particles were weakly flocculated (by salt in the case of o/w [35] or by surfactant in the case of w/o [36]); less stable emulsions resulted when the particles were completely flocculated. Hydrophilic fumed silica (Aerosil 200, primary particle diameter = 12 nm) was chosen for study and, by raising the pH, the particles were rendered negatively charged to their highest extent due to ionisation of surface silanol (SiOH) groups [19]. The flocculation of aqueous colloids on addition of increasing concentrations of 3:1 electrolyte lanthanum chloride was monitored using turbidity. At pH 10, the turbidity increased by a factor of three on addition of 20 mM LaCl_3 with the colloids separating into a clear upper layer and a turbid lower layer for $[\text{LaCl}_3] \geq 1$ mM. The stability of the corresponding o/w emulsions is very dependent on salt concentration as shown in Fig. 4, where it can be seen that the stability to both creaming (open points) and coalescence (filled points) passes through a marked maximum at intermediate concentrations at approximately 2–5 mM decreasing sharply either side of this range. These emulsions remained at this stability for over one year, and the example demonstrates that an otherwise poor stabilising system (hydrophilic silica in pure water) can be made optimally stable with low levels of salt.

Below 2 mM LaCl_3 , rapid creaming occurred in which the resolved aqueous phase was clear blue. Between 2 and 5 mM, the small volume of aqueous phase resolved was colourless, implying that the particles originally present in water

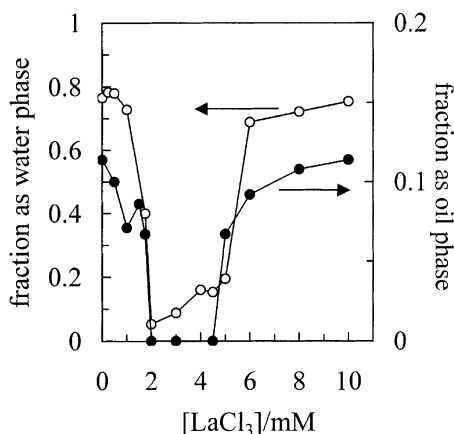


Fig. 4. Stability to creaming (open points, left hand ordinate) and coalescence (filled points, right hand ordinate) after 30 min of 20 vol.% toluene-in-water emulsions stabilised by 0.5 wt.% hydrophilic silica particles as a function of LaCl_3 concentration at pH 10. Taken from ref. [19].

transferred into either the dispersed oil phase or to the oil–water interface. Above 6 mM, the resolved aqueous phase was viscous and turbid and most likely contained flocculated particles. The marked increase in turbidity of the colloids occurs between 1 and 2 mM salt marking the onset of flocculation. This is exactly where the emulsion stability begins to increase drastically. The appearance of flocculated particles initially enhances the emulsion stability. Further increase in salt concentration results in destabilisation. It may be that small flocs if formed at low salt concentration adsorb to drop interfaces resulting in stabilisation, whereas at higher salt concentration the floc size and extent may be larger and adsorption is reduced. Our finding that partial flocculation, i.e. moderately prevalent attraction between the particles, is necessary for emulsion stabilisation agrees with the conclusions of Lucassen-Reynders and van den Tempel [36] on the effect of added surfactant on the stability of w/o emulsions containing glycerol tristearate crystals. A theoretical description of the adsorption of charged particles to charged liquid surfaces concludes that adsorption is favoured in the presence of salt as particles become more hydrophobic [30]. Similar findings to those of silica were reported for o/w emulsions stabilised by 30 nm diameter disc-shaped hydrophilic clay particles [24].

2.3. Catastrophic inversion

Phase inversion of emulsions, from w/o to o/w or vice versa, can be achieved in surfactant-stabilised systems by changing the oil/water volume ratio. We have argued that this type of conversion, known as catastrophic inversion [37], only occurs in emulsions containing surfactant and cosurfactant and is accompanied by dramatic changes in properties of the emulsions, including viscosity and drop size. It is believed that the spontaneous curvature of the mixed surfactant-cosurfactant

layer around drops changes with the oil/water ratio due to a change in the composition of the layer after partitioning between bulk phases is complete. One emulsion type is then favoured over the other as the volume fraction of, say, water (ϕ_w) is increased. In emulsions stabilised by only one pure surfactant, inversion does not occur; instead high internal phase gel emulsions form upon increasing the volume fraction of dispersed phase [22].

We have been fortunate to have had synthesised by Wacker-Chemie (Munich) a series of fumed silica particles of the same size distribution but of increasing hydrophobicity, achieved by controlled reaction of hydrophilic silica with dichlorodimethylsilane in the vapour phase. Although the primary particle diameter varies between 10 and 30 nm, silica particles aggregate easily or fuse completely to give larger structures of non-spherical shape [38]. The hydrophobicity of the particles, qualitatively assessed via powder immersion measurements [23], is described in terms of the percentage of silanol groups on their surface. Thus, raw hydrophilic silica possesses 100% SiOH and the most hydrophobic has 14% SiOH. The silane coating is assumed to be homogeneous over the particle surface. More hydrophilic particles ($> 65\%$ SiOH) can be dispersed in water using ultrasound, whereas more hydrophobic ones are easily dispersed in oil. Preferred emulsions, i.e. those formed at an oil/water volume ratio of unity, are o/w for the hydrophilic silicas and w/o for the hydrophobic ones, in line with previous findings for large glass particles [39]. However, in one and the same system, emulsions of both types can be prepared depending on the oil/water ratio [20].

The photograph of the emulsions in Fig. 5 (upper) gives an example of phase inversion induced by increasing the volume fraction of water in pure cyclic silicone oil systems stabilised by silica particles possessing 57% SiOH [31]. At constant particle concentration initially in oil (2 wt.%), emulsions invert from w/o (3 on left) to o/w (3 on right) between $\phi_w = 0.65$ and 0.70. Although all these emulsions are completely stable to coalescence, oil external emulsions do not sediment whereas water external ones cream under gravity. In the example given in Fig. 5 (lower), emulsions are of low conductivity and disperse in oil at low ϕ_w (w/o) but become highly conducting dispersing in water at high ϕ_w (o/w). The experiment was carried out in four ways with the results being virtually identical. Emulsions were prepared by either sequential addition of water to toluene (open points) or by sequential addition of toluene to water (filled points), the oil containing 2 wt.% particles in both cases. Emulsions were also prepared separately at each ϕ_w by direct mixing of the components, for both a fixed particle concentration in oil and a constant particle concentration in all emulsions (not shown). The agreement between the data sets is encouraging and confirms that, irrespective of the route or overall particle concentration, phase inversion can be achieved without altering the particle wettability.

Both emulsion types are stable to coalescence for periods in excess of 3 years, despite being of very different average drop diameter, namely 1 (w/o) and 100 (o/w) μm . The ability to make both types of emulsion with the same kind of particles represents a significant advantage compared with single surfactant systems. Inversion

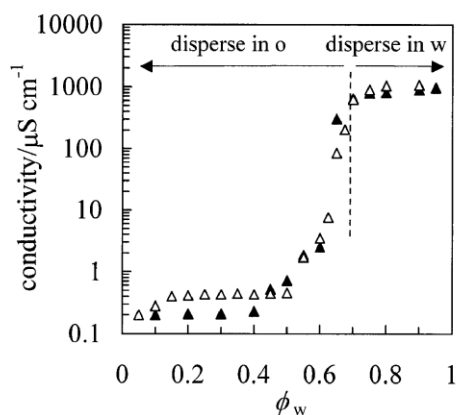
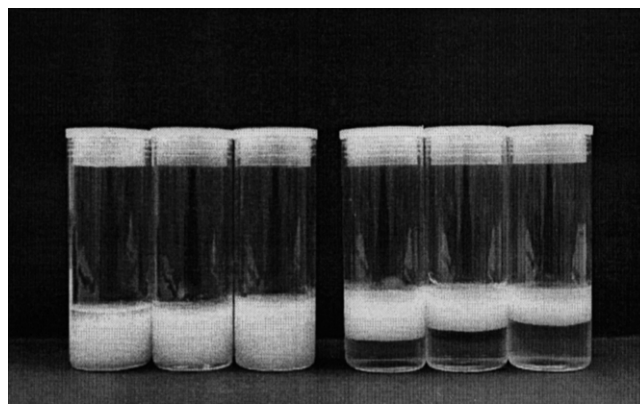


Fig. 5. (upper) Appearance of emulsions immediately after preparation in the system decamethylcyclotrioxane-water-silica particles of intermediate hydrophobicity. The values of ϕ_w are (left to right) 0.4, 0.6, 0.65, 0.7, 0.8, 0.9, with the gap separating w/o emulsions on left from o/w emulsions on right. Taken from ref. [31]. (lower) Conductivity and drop test result of water-toluene emulsions stabilised by 2 wt.% hydrophobic silica particles (50% SiOH) in oil as a function of the water volume fraction. Open points—water added sequentially to oil; filled points—oil added sequentially to water. Taken from ref. [20].

occurs without hysteresis (increasing or decreasing ϕ_w) in contrast to surfactant systems where the hysteresis can be as much as 0.3 in volume fraction. In addition, emulsions are most stable at conditions near inversion unlike those of surfactants, which are notoriously very unstable. This is illustrated in Fig. 6 for the same system as in Fig. 5 (lower), where the stability to sedimentation of w/o emulsions increases towards inversion as does the stability to creaming of the o/w emulsions. The large difference in the relative stabilities of the two emulsion types is due in part to the difference in drop size. Repeating the measurements using particles of different silanol content reveals that the value of ϕ_w at inversion increases progressively with

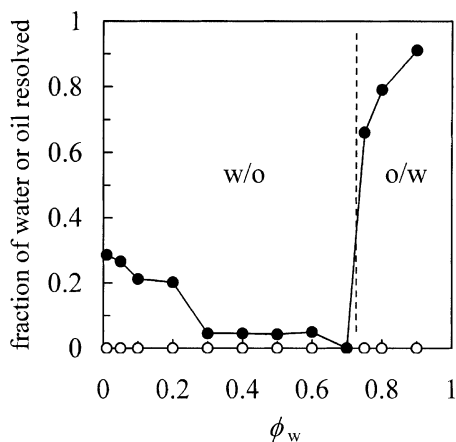


Fig. 6. Stability after 1 h of water–toluene emulsions stabilised by 2 wt.% hydrophobic silica particles (50% SiOH) in oil as a function of ϕ_w . Open points refer to coalescence; filled points refer to sedimentation for w/o and creaming for o/w. Taken from ref. [20].

particle hydrophobicity, varying from 0.35 to over 0.8 [23]. It remains to understand why both types of emulsion occur in systems containing the same three components (oil, water, solid).

2.4. Rheology of emulsions

One interesting feature of silica-stabilised emulsions is their very high viscosity at relatively low particle concentrations (few wt.%). The rheology is due not only to the fact that drops are coated with solid particles but that the continuous phase can be made viscous due to aggregation of excess particles. In some cases, an emulsion has the consistency of a cream and does not flow even at low dispersed phase volume fraction. For the emulsions described in Fig. 6 undergoing catastrophic inversion it was observed visually that the viscosity passed through a maximum near the inversion condition. Using a controlled shear rate rheometer, the absolute viscosity of such emulsions was determined as a function of shear rate with a double concentric cylinder cell. All emulsions exhibited shear-thinning (viscosity decreasing with shear rate) up to a shear rate plateau of approximately 800 s^{-1} probably as a result of the shear disrupting flocculated drops. The emulsion viscosity is shown as a function of ϕ_w for two different shear rates (below and above the plateau) in Fig. 7 for toluene–water emulsions containing 1 wt.% of particles in each emulsion. Interestingly, the maximum in viscosity occurring at $\phi_w = 0.55$ does not coincide with the volume fraction of water at phase inversion, 0.70. In surfactant systems [40], the viscosity increases continuously with dispersed phase volume fraction towards inversion for both emulsion types.

A tentative explanation for the mismatch in the particle emulsions involves consideration of changes in the drop size distribution with ϕ_w . As detailed earlier

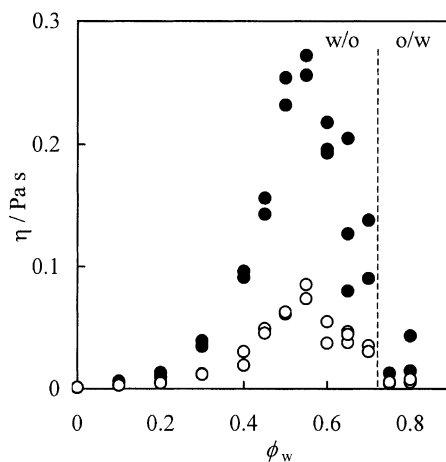


Fig. 7. Absolute viscosity of toluene–water emulsions stabilised by hydrophobic silica particles (50% SiOH, 1% wt./vol. in each) as a function of water volume fraction for shear rates of 184 (filled points) and 921 (open points) s^{-1} . Dotted line indicates condition of phase inversion. Taken from Binks et al., unpublished.

[20], w/o emulsions at low ϕ_w were of monomodal size distribution centred approximately $0.7 \mu\text{m}$ diameter. At higher ϕ_w values (0.5, 0.6), a shoulder appears in the w/o distributions at larger drop diameters at approximately $20 \mu\text{m}$, amounting to 15 vol.% of the total number of drops. The corresponding viscosities are lower than predicted on the basis of the increased dispersed phase volume fraction. It is suggested that the increased polydispersity of these emulsions is the cause. It is well known for particle suspensions that the size distribution has a major effect on the suspension viscosity particularly at solid volume fractions above 0.5. Chong et al. [41], using mixtures of monodisperse particles of different sizes, showed that the viscosity decreased by over an order of magnitude on adding 25% of larger particles (ten times the diameter) to a suspension of small particles. The o/w emulsions formed at $\phi_w > 0.7$ are of low viscosity consistent with them being relatively dilute and containing large drops ($100 \mu\text{m}$).

2.5. Transitional inversion

An alternative type of emulsion transformation is known as transitional inversion [37], brought about by changing the HLB of the system in some way at fixed volume fraction of oil and water, e.g. by increasing the concentration of hydrophobic cosurfactant in monolayers of hydrophilic surfactant. For particles, the equivalent HLB scale can be thought of as the particle wettability. In a study into the effect of silica particle hydrophobicity on the type and stability of toluene-containing emulsions [23], it was shown that predictions based on considerations of the energy of attachment of a single particle to the oil–water interface, Eq. (1), relate directly

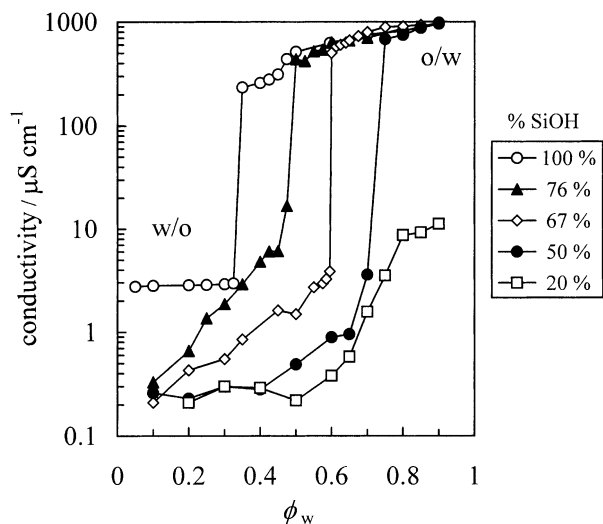


Fig. 8. Conductivity and type of water–toluene emulsions stabilised by silica particles of different hydrophobicity (given) as a function of the volume fraction of water. Taken from ref. [23].

to the stability of emulsions. From the catastrophic inversion plots in Fig. 8, it can be seen that emulsions at $\phi_w=0.5$ are w/o for hydrophobic particles (low SiOH) and o/w for hydrophilic particles (high SiOH). Thus, one way to effect transitional inversion is to simply decrease the silanol content on the particles. Table 2 summarises the stability and drop sizes of emulsions in such an experiment. Emulsions stabilised by very hydrophilic or very hydrophobic particles contain large drops ($> 100 \mu\text{m}$) and are unstable to coalescence, presumably as a result of their facile displacement from interfaces during drop collisions. Those with particles of

Table 2

Summary of stability to coalescence and median drop diameter of preferred water–toluene emulsions, $\phi_w=0.5$, stabilised by silica particles of different hydrophobicity^a. Taken from ref. [23]

% SiOH	Type	Median diameter/ μm	Variable [particles]		Fixed [particles]	
			% Coalescence	Time	% Coalescence	Time
100	o/w	150	30 ^b	2 min	90	2 min
79	o/w	120	5	10 min	5	8 min
76	o/w	75	0	3 years	0	3 years
67	w/o	1	0	3 years	0	3 years
50	w/o	0.7	0	3 years	0	3 years
20	w/o	200	46 ^c	2 min	89	2 min

^a Coalescence extent within a certain time is shown for experiments in which particle concentration in emulsions varies with particle hydrophobicity and in which it remains constant at 1 wt.%.

^b Coalescence continues to increase to approximately 80% over 1 h.

^c Coalescence remains at this value indefinitely.

intermediate hydrophobicity, in which particles are held strongly at interfaces, contain sub-micron sized drops and are stable to coalescence indefinitely. Unlike coalescence that either occurs or does not within the particle series, the stability to gravity-induced separation (creaming for o/w and sedimentation for w/o) passes through a sharp maximum upon increasing the particle hydrophobicity. In line with this, the average drop size passes through a minimum. This correspondence is shown to be universal and independent of both ϕ_w and the type of emulsion formed.

An alternative way to induce transitional inversion is to stabilise emulsions ($\phi_w = 0.5$) using mixtures of particles of different hydrophobicity, one type of which prefers o/w emulsions and the other w/o emulsions. The possibility of gradually changing the average wettability of the particles at the drop interfaces therefore exists. Three ways of achieving this are by addition of hydrophilic silica particles to w/o emulsions stabilised by hydrophobic silica, by addition of hydrophobic silica to o/w emulsions stabilised by hydrophilic silica and by varying the weight fraction of one of the particle types at constant particle concentration [21]. Fig. 9 presents plots of the emulsion conductivity as a function of the concentration of added particles of the second type, prepared as batch emulsions. As predicted, inversion occurs in both directions depending on whether the starting emulsion is w/o (upper) or o/w (lower). Although both types of emulsion containing particle mixtures are very stable to coalescence, the stability to creaming of o/w and sedimentation of w/o emulsions decreases approaching the conditions of inversion, consistent with the median drop sizes displaying a maximum (Fig. 10). This is exactly the opposite behaviour to that described above in which inversion occurs in systems of one particle type by varying the inherent hydrophobicity of the particles.

It is assumed in the above that the average wettability of the particles at the oil–water interface in mixtures changes, say, from mainly water wettable to mainly oil wettable as the proportion of hydrophobic particles in the system increases. That this is reasonable is supported by contact angle data of Diggins et al. [42] who measured the wettability of quartz powders (59 μm diameter) in air via capillary pressure determinations. Their data, given as the inset in Fig. 10, shows that the contact angle decreases nearly linearly with the volume fraction of hydrophilic powder in mixed beds with hydrophobic powder. Although the data refer to an air–water surface, the corresponding angles at the oil–water interface will all be higher than those shown and it may be that inversion to o/w emulsions occurs at conditions where the average contact angle passes through 90° . Returning to the different trends in emulsion stability depending on the variable inducing inversion, it is likely that the packing of particles around drops is disrupted upon incorporating other particles of different wettability.

2.6. Influence of particle location

One of the intermediate silica particle types mentioned above contained 67% SiOH on its surface and very stable, sub-micron diameter emulsions could be prepared. Being of intermediate hydrophobicity, it could be imagined that emulsions stabilised by these particles would be very sensitive to prevailing conditions. Such

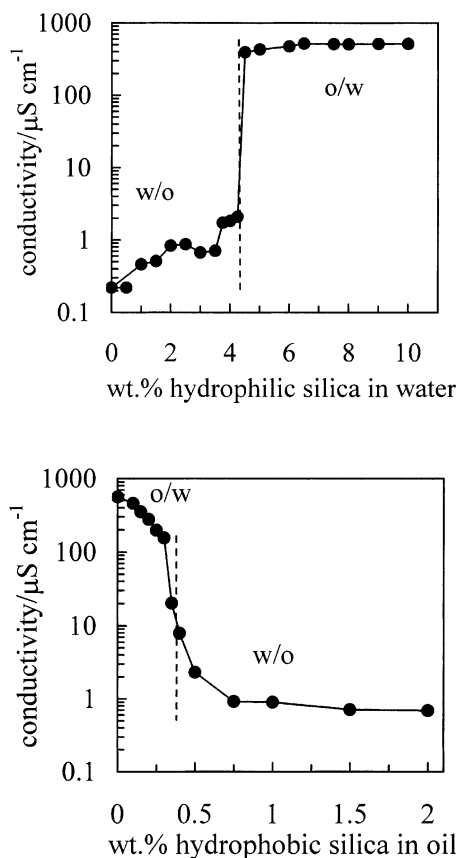


Fig. 9. (upper) Conductivity and type of water–toluene emulsions ($\phi_w=0.5$) containing 2 wt.% hydrophobic silica particles in oil (fixed) as a function of added hydrophilic particles in water. (lower) Conductivity and type of water–toluene emulsions ($\phi_w=0.5$) containing 2 wt.% hydrophilic silica particles in water (fixed) as a function of added hydrophobic particles in oil. Taken from ref. [21].

particles can be dispersed separately in either oil or water phases and it is of interest to investigate the effect of the initial location of the particles on emulsion type and stability. Since particles are significantly larger than surfactant molecules, the question arises whether they equilibrate between the bulk phases and interface to the same extent in both situations. Fig. 11 reveals that catastrophic phase inversion in toluene-containing emulsions is dependent on the initial state of the system [22]. For particles originally dispersed in water (open points), ϕ_w at inversion is 0.35, compared with a value of 0.60 when starting in oil (filled points). If an equal mass of particles is dispersed in both oil and water phases before emulsification, an intermediate value of 0.45 is obtained. The continuous phase of the preferred emulsion thus becomes that in which the particles are first dispersed. The same result has recently been confirmed in silica particle–water–triglyceride oil emulsions

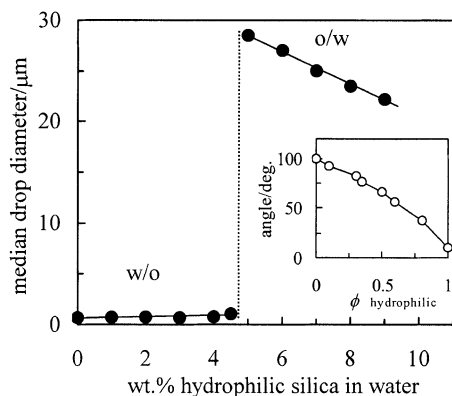


Fig. 10. Median drop diameter of w/o and o/w emulsions containing toluene stabilised by mixtures of hydrophobic and hydrophilic silica particles. Taken from ref. [21]. Inset shows the variation of the contact angle of a water drop in air in a packed bed of mixtures of hydrophilic and hydrophobic quartz particles as a function of the volume fraction of hydrophilic particles (from ref. [42]).

and so appears generic [31]. A possible explanation for this phenomenon may be linked to the different contact angles the particles adopt at the interface in one and the same system, i.e. hysteresis caused by particle surface roughness. For particles entering the interface from water, a receding angle (measured into water) is probably established whereas an advancing angle (measured into water) is more likely when particles are adsorbed from oil. Since receding angles are normally smaller than advancing ones, the same particle behaves as if more hydrophilic (preferring o/w emulsions) in the former case and more hydrophobic (preferring w/o emulsions)

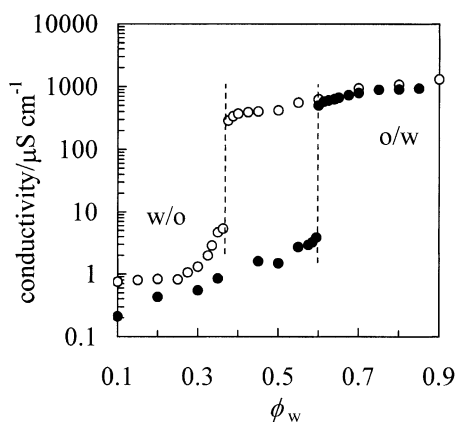


Fig. 11. Conductivity and type of water-toluene emulsions stabilised by 0.5 wt.% silica particles of intermediate hydrophobicity (67% SiOH) vs. the volume fraction of water. Open points—particles initially dispersed in water; filled points—particles initially dispersed in oil. Taken from ref. [22].

in the latter case. In addition, contact angles of water drops on planar, partially hydrophobised glass slides (akin to particle surfaces) are always higher by approximately 25° when oil contacts the substrate first [31]. Clearly, particle–fluid interactions are important prior to the introduction of the second fluid phase.

It was also established that preferred emulsions were composed of smaller drops than non-preferred emulsions (o/w if starting in oil and w/o if starting in water). An important conclusion arising from this work is that maximum stability can be obtained for either emulsion type simply by changing the initial particle location. In contrast, evidence was given that emulsion type is independent of initial location for surfactant-stabilised systems due to the faster distribution of molecules between phases occurring during formation.

2.7. *Effect of oil type*

In surfactant systems, preferred emulsions can be of either type depending on the chemical structure of the oil. For example, short chain alkanes favour w/o emulsions whereas long chain alkanes favour o/w emulsions. The preference is explained in terms of the different penetration extents of oil into the chain region of surfactant monolayers and the subsequent influence on the spontaneous curvature of the layers. Small molecule oils swell the chain region more than longer homologues producing layers of more negative curvature [43]. For solid particles as emulsifiers, the chemical interactions between the solid surface and the two liquid phases, which ultimately determine the contact angle θ_{ow} , need to be taken into account. The effect of oil type on emulsions stabilised by partially hydrophobic silica particles (67% SiOH) was combined with measurements of the contact angles of water drops under oil phases on hydrophobised glass plates [22]. Since the energy of attachment of particles anchored at interfaces depends on both θ_{ow} and the oil–water tension γ_{ow} , the influence of both parameters on emulsion behaviour can be assessed. The oils ranged from non-polar hydrocarbons of relatively high γ_{ow} to polar alcohols and esters of relatively low γ_{ow} . It turned out that particles are more hydrophobic (higher θ_{ow}) at polar oil–water interfaces preferring w/o emulsions, and are more hydrophilic (lower θ_{ow}) at non-polar oil–water interfaces with preferred emulsion type being o/w. This is easily seen in the plots of the emulsion conductivity (and drop test outcome) as a function of ϕ_w for different oils given in Fig. 12. Inversion does not occur for certain oils, e.g. eugenol, and occurs at different values of ϕ_w for other oils. The combination of a low tension (9.5 mN m^{-1}) and high contact angle (160°) in the case of undecanol leads to an unusual phenomenon in which initially stable w/o emulsions destabilise completely into the parent liquid phases with time. The breaking of the emulsion is such that it contracts via coalescence in a way that maintains the shape of the vessel. A similar instability process was reported by Philip et al. [44] for viscous bitumen-in-water emulsions and is reminiscent of the sintering process which occurs during the densification of powders.

In a theoretical paper, Binks and Clint [25] used surface energy considerations to interpret the interactions between the three phases and hence to predict γ_{ow} in the

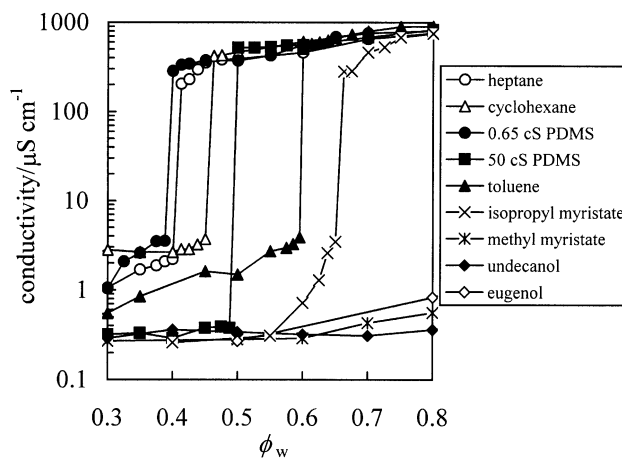


Fig. 12. Conductivity of water–oil (given) emulsions stabilised by partially hydrophobic silica particles (67% SiOH) as a function of the volume fraction of water. Concentration of particles in all emulsions is 0.5 wt./vol.%. Taken from ref. [22].

cases above. Such approaches, where surface energies are split into components reflecting different types of intermolecular forces, are gaining increasing acceptance for a variety of applications. For a solid particle (s) located at the oil (o)-water (w) interface, the three interfacial tensions (γ) are related to the contact angle θ_{ow} by the Young equation

$$\gamma_{so} - \gamma_{sw} = \gamma_{ow} \cos\theta_{ow} \quad (2)$$

Although the interfacial tension γ_{ow} can be measured accurately, there are no direct methods for measuring γ_{so} and γ_{sw} . It would clearly be helpful to be able to use Eq. (2) to predict values for the contact angle if it were possible to estimate all three tensions from some other source of data. This would require the use of combining rules that allow any interfacial tension to be predicted from ‘surface tension components’ and the determination of such components for solid surfaces. A commonly used approach to this is to express any surface tension as a sum of components due to dispersion forces and polar forces [45]. Based on this, our procedure was to first calculate the surface energy components for an oil phase from a knowledge of its surface tension against air and its interfacial tension against water. The magnitude of the polar component broadly reflects the chemical groups present in the molecules, being especially large for alcohols as a result of the OH groups. The equivalent components of the surface energy of a particular solid are then calculated from contact angle data for water in air and under a chosen oil. Finally, the component energies of both the oil and solid phases are used to calculate theoretical values of the oil–water contact angle using Eq. (2) and suitable versions of the combining equations.

The calculated values of θ_{ow} are shown in comparison with the experimental values in Fig. 13 for nine different oils on seven different solid surface types, where

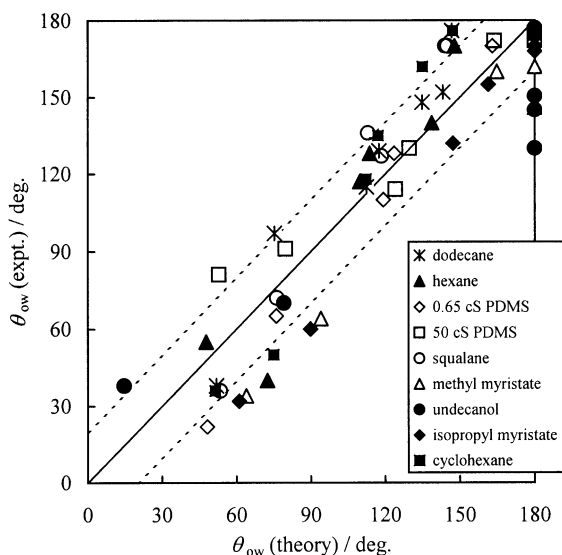


Fig. 13. Experimental (ordinate) vs. calculated (abscissa) contact angles of water drops under nine different oils on seven different solid surfaces, including silicon wafer, hydrophilic glass, hydrophobic glass, polystyrene, polyvinyl chloride, polymethylmethacrylate, polytetrafluoroethylene. The diagonal full line indicates agreement between theory and experiment. Taken from refs. [10,22,25].

the full diagonal line represents agreement between the two. The majority of the points fall within 20° of the line, lending support to the approach taken. Some points for undecanol (filled circles) lie well away from the line and we argued that, unlike non-polar oils, alcohol molecules can be adsorbed at some or all of the three interfaces involved in the wetting. Although at oil–water and solid–water interfaces, the likely orientation is with the polar $-\text{OH}$ group in water, the situation is less clear at the solid–oil interface. This may be the cause of the lack of agreement with what is essentially a simple treatment of intermolecular interactions. The approach was also extended to model silica surfaces of different hydrophobicity. On the assumption that the variation of the solid surface energy components varied linearly with silanol content (from the extremes of clean glass to a silicone oil surface), we showed that to effect inversion (θ_{ow} to pass through 90°), silica surfaces of increasing hydrophilicity require oils of increasing polarity. A strength of the approach is that the type of emulsion, stabilised only by solid particles of known surface energy components, as judged by θ_{ow} , can be predicted knowing only the surface tension of the oil in air and its interfacial tension with water.

2.8. Interfacial structure

Since sub-micron sized particles adsorbed at emulsion drop interfaces cannot be visualised using optical microscopy, the technique of freeze fracture scanning electron microscopy (SEM) has been applied to these systems [29]. The procedure

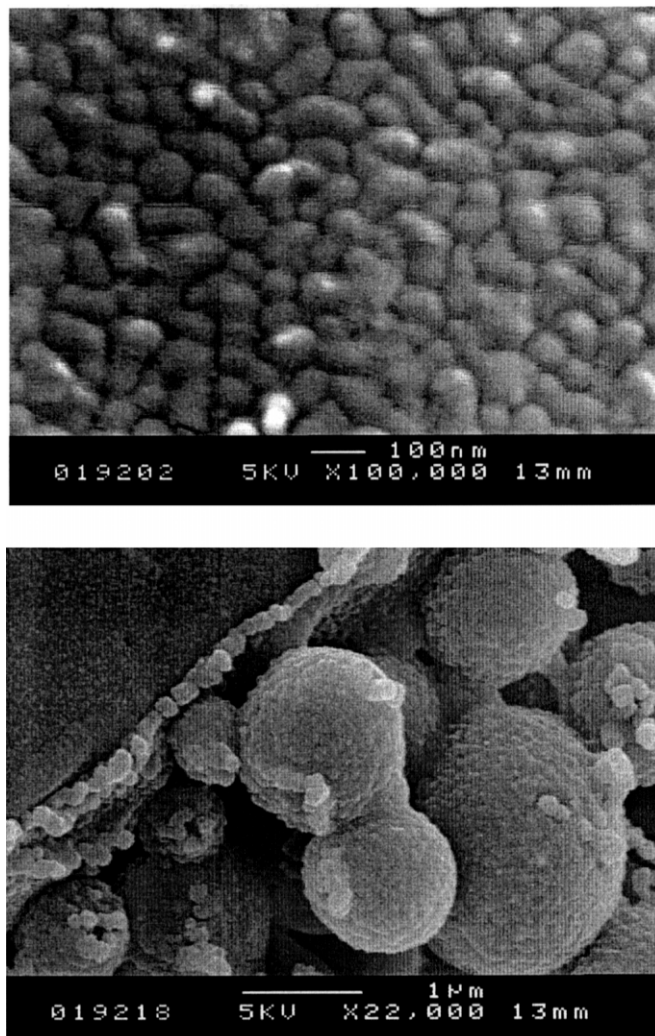


Fig. 14. Freeze fracture SEM images: (upper) A triglyceride-in-water emulsion stabilised by silica particles of intermediate hydrophobicity. The close-packed arrangement of particles on the external surface of a drop is viewed from the continuous phase; (lower) A water-in-cyclohexane emulsion stabilised by 0.21 μm diameter polystyrene sulfate latex particles. Taken from ref. [29].

involves plunging a freshly prepared emulsion sample into liquid nitrogen at -196 $^{\circ}\text{C}$. The frozen sample is rapidly transferred to an evacuated, low temperature preparation chamber where it is fractured, coated with a mixture of gold and palladium and observed on the cold stage of a field emission scanning electron microscope. Examples of images obtained with this protocol are given in Fig. 14. The upper image originates from a medium chain triglyceride-in-water emulsion

stabilised by silica particles of intermediate hydrophobicity. It shows the external surface of an oil drop viewed from the continuous aqueous phase. The absence of any holes in the particle layer is most likely due to the polydispersity in size and to the different shapes of the particles leading to very efficient packing. It should be noted, however, that the average ‘size’ of the individual particles (60–80 nm) is larger than the primary particle diameter (20 nm) suggesting fusion has taken place between particles in close proximity. This is a common feature of fumed silica particles in either the vapour phase or in liquid dispersions. In other o/w emulsions of silica, the arrangement of particles at drop interfaces was in the form of flocs of particles separated by particle-free regions, however.

The lower image in Fig. 14 is that of a water-in-cyclohexane emulsion stabilised by 0.21 μm diameter monodisperse polystyrene sulfate latex particles. In this case the oil has been sublimed leaving voids between drops. The average drop diameter (1 μm) agrees with that measured previously by light diffraction. Part of a larger drop can be seen in the top left of the image and individual particles (white objects) are visible forming a monolayer at the water–void (cyclohexane) interface. The surfaces of the smaller drops have a distinctly ‘knobbly’ appearance due to close-packed adsorbed particles, and several excess particles exist above this surface originating in the continuous phase and left behind after sublimation of the oil. The particles, of original diameter equal to 0.21 μm , are reassuringly approximately 200 nm in diameter but some appear to have shrunk slightly and assumed a non-spherical shape. Behaviour of this kind with polystyrene particles is not unexpected as a result of the overall process of freezing, fracturing and sublimation under vacuum. These first micrographs of particles at curved emulsion drop interfaces raise many questions, which are worth pursuing with further experiments.

3. Multiple emulsions

In addition to acting as emulsifiers in simple emulsions, the possibility exists that particles may be effective at stabilising multiple or double emulsions. The latter have been termed ‘emulsions of emulsions’, i.e. the globules of the dispersed phase contain even smaller dispersed droplets themselves. In the surfactant case, two different surfactants are normally required in order to prepare such emulsions, one of which adsorbs primarily at the interface of inner drops whilst the other adsorbs mainly at the outer globule interface [46]. Since the curvatures of the two types of monolayer are opposite, a mixture of a hydrophilic and a hydrophobic surfactant is used to satisfy this requirement. Tween (hydrophilic) and Span (hydrophobic) surfactants are popular choices in this respect. Thus, for oil-in-water-in-oil (o/w/o) emulsions, it is normal practice to prepare an o/w emulsion with the hydrophilic surfactant which is then re-emulsified gently into an oil phase containing dissolved hydrophobic surfactant. However, the main problem associated with surfactant-stabilised emulsions so far and which has prevented their widespread use commercially, is their inherent instability as a result of coalescence leading ultimately to the formation of a simple emulsion. Some attempts have been made at improving the shelf-life of multiple emulsions by incorporating small solid particles into the

surfactant formulations. The idea, as before, is that particles act as a mechanical barrier to coalescence if adsorbed at interfaces. Oza and Frank [47] were the first to develop this by using colloidal microcrystalline cellulose (MCC) as the water-soluble emulsifier in water-in-oil-in-water (w/o/w) emulsions containing oil-soluble Span surfactants. Emulsions, stable for up to 1 month, contained a network of MCC adsorbed at the outer oil–water interface. Subsequently, Garti et al. [48] demonstrated the enhancement in stability to coalescence on addition of sub-micron crystalline fat particles as a co-stabiliser of the inner interface of water-in-soybean oil-in-water emulsions. A similar improvement in stability but for o/w/o emulsions was reported by Sekine et al. [49] in which the external w/o interface was partially coated with a layer of hydrophobically modified clay particles causing it to become rigid. The organoclay particles also caused gelling of the outer oil phase preventing sedimentation of the water globules. Unlike the above studies in which both surfactants and particles have been employed in combination, Binks et al. [27,28] have successfully prepared multiple emulsions using particles alone as emulsifier. It is predicted that multiple emulsions should form in oil+water mixtures containing two types of particles differing only in their hydrophobicity. In practice this turns out to be the case and extremely stable multiple emulsions of both types are possible using a mixture of silica particles differing by only 25% in SiOH content. This novel class of multiple emulsions should prove of great benefit in the pharmaceutical field where controlled release of substances is required in certain applications.

3.1. Water-in-oil-in-water

Multiple w/o/w emulsions with either toluene or triglyceride oil were prepared in a two-stage process. The first step involved the formation of a w/o emulsion by homogenising water ($\phi_w=0.2$) into a dispersion of hydrophobic silica particles in oil with high shear. In the second step, the w/o emulsion just made was re-emulsified into an aqueous dispersion of hydrophilic silica particles using low shear. The volume fraction of w/o emulsion in the final multiple emulsion was also 0.2. An example of such an emulsion is shown in Fig. 15 (upper) in which oil globules are approximately 40 μm in diameter and water drops are 2 μm . We find that a minimum concentration of both particle types is required for the formation of multiple emulsions, below which only simple emulsions exist. Increasing the concentration of inner hydrophobic silica leads to an increase in the average globule diameter alongwith an increase in the number of inner water drops per globule. By contrast, an increase in the outer hydrophilic silica concentration causes the globule diameter to decrease and the viscosity of the outer water phase to increase. Both drops and globules are stable to coalescence for over 1 year in all emulsions; typically 2 wt.% of each particle type is sufficient to produce w/o/w emulsions, which do not cream or coalesce with time. Since the migration of particles from inner to outer interfaces or vice versa is expected to be minimal after emulsion formation, the major cause of instability occurring in surfactant emulsions is removed. We have also studied the kinetics of release of electrolyte from inner drops to the outer aqueous phase under isotonic conditions in w/o/w emulsions of

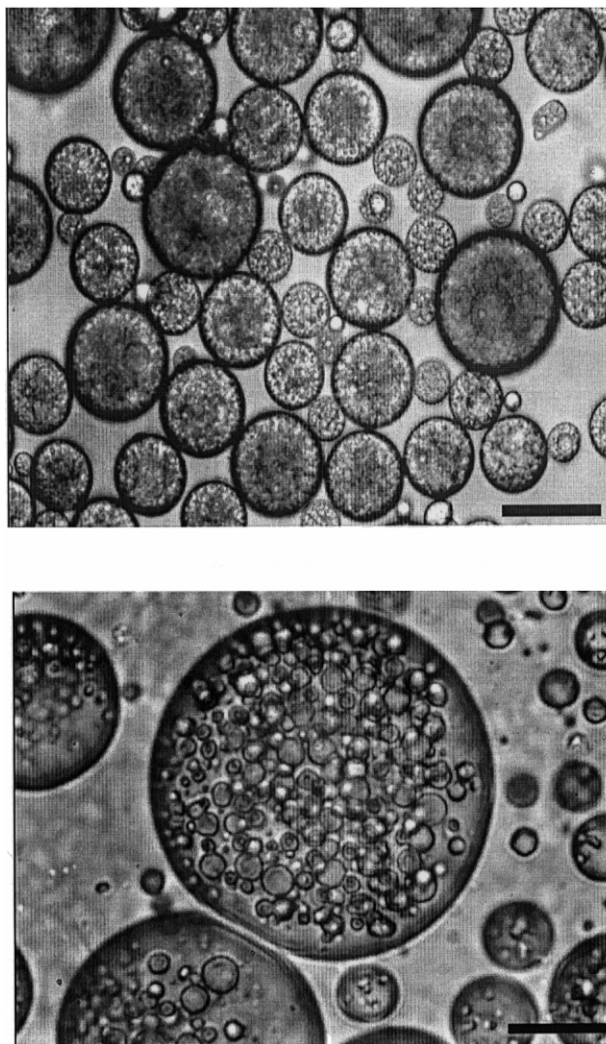


Fig. 15. Optical microscopy images of multiple emulsions stabilised entirely by two types of silica particles of different hydrophobicity: (upper) w/o/w with triglyceride oil and bar=50 μm ; (lower) o/w/o with toluene and bar=20 μm . Taken from refs. [27,28].

toluene using conductivity [28]. A model in which the diffusion of salt through the oil membrane including its partitioning between water and oil has been put forward. The calculated rate constant for release however is much larger than the experimental first-order one suggesting that either an energy barrier to the interfacial transport of salt is present or that counter transport of glucose (required to maintain isotonicity) from outer to inner aqueous phases is significant.

3.2. Oil-in-water-in-oil

In a similar manner, o/w/o emulsions were prepared by first emulsifying oil into an aqueous dispersion of hydrophilic silica particles, and then gently re-emulsifying the o/w emulsion so formed into an oil dispersion of hydrophobic silica particles. Fig. 15 (lower) shows a typical microscopic image of a multiple emulsion with toluene as oil, where the contrast is improved. The effects of particle concentration, oil type and oil/water ratio have been investigated and, as before, emulsions stable to both coalescence and sedimentation can be prepared at high enough concentrations of the two particle types. We hope to verify that inner and outer interfaces are coated separately by only one particle type by using large fluorescent particles visible by microscopy.

4. New materials from solid-stabilised emulsion templates

In other work, we have been studying the kinetics and mechanism of evaporation of water and oil from creamed o/w emulsions stabilised by various surfactants [50]. Evaporation rates are of interest in many contexts including assessment of hazards from the spillage of volatile chemicals, drying processes and the release of volatile active species such as perfumes and flavours from cosmetic and food products. It is found that the continuous aqueous phase of the emulsions evaporates at a rate equal to that for pure water under the same conditions of controlled gas flow. The evaporation rate of dispersed, oil however, is retarded relative to non-emulsified oil, by a factor ranging from 1 to 20 depending on the oil type. The main factor slowing down the loss is the water solubility of the oil, with retardation increasing as the water solubility decreases. The data were analysed in terms of a model in which oil evaporation proceeds by a mechanism of diffusion of dissolved oil across the thin water film present at the emulsion surface.

In a continuation of this work with silica-stabilised o/w emulsions, the main effect of replacing surfactant by particles is to reduce still further the evaporation of oil. However, after a sufficiently long time such that both liquids have evaporated, a solid residue remains composed of silica particles in some form of aggregated structure from these and corresponding w/o emulsions. Porous inorganic materials possess a unique set of properties including high specific stiffness, high damping capacity, high thermal shock resistance and high surface area. Consequently they are used in either structural or functional applications such as high temperature insulation, catalyst supports, gas and moisture sensors. Processing methods for cellular inorganic materials like silica or zirconia include foaming of molten glasses and cements, sintering of hollow glass spheres and foaming of sol–gel systems [51]. The possibility arises that, depending on exactly how oil and water are lost, solid-stabilised emulsions can be used as templates for the initial ordering of particles around drops and the subsequent formation of new porous solid phases.

4.1. Emulsions stabilised by particles of two types

We described above the inversion of equal volume oil and water emulsions by increasing the proportion of, say, hydrophobic particles in mixtures with hydrophilic

particles. A new set of emulsions was prepared containing a total of 5 wt.% particles starting with between 0 and 5 wt.% hydrophilic particles in water and between 5 and 0 wt.% hydrophobic particles in toluene respectively [32]. On drying, it was noticed that emulsions rich in hydrophobic particles were w/o and left a clear, rubbery gel of the same shape as the cuvette they were placed in originally. Emulsions rich in hydrophilic particles were o/w and, following the same amount of time left open as before, gave clear blue aqueous dispersions. For compositions around phase inversion (near equal amounts of both particle types), an opalescent solid tablet phase appeared of cylindrical shape like the container. Exposing a fresh fracture surface at the top of such a sample by gentle scraping and coating with a thin layer of carbon produced the SEM image shown in Fig. 16 (upper) from a w/o emulsion close to inversion. A porous, sponge-like structure is very evident in which the primary particles have fused into larger agglomerates and a labyrinth network of solid layers progresses through the sample. Although on a different length scale, the image is reminiscent of cryo-transmission electron microscopy images of bicontinuous microemulsions containing equal volumes of oil and water separated by fluctuating monolayers of surfactant [52]. The latter contain regions of positive curvature (around oil domains) and regions of negative curvature (around water domains) with the overall net curvature being close to zero. Since we suggested that the average wettability of the particles at the oil–water interface changes from, say, oil wettable to water wettable accompanying inversion in mixtures, the structure of the solid phase after evaporation may be comprised of regions of predominantly hydrophobic particles (curvature one way) and regions of predominantly hydrophilic particles (curvature the other way). This appears to be another example of the similarity between particles and surfactants in oil + water systems. A completely different structure is formed from a toluene-in-water emulsion rich in hydrophilic silica particles at higher overall total particle concentration than above. As seen in Fig. 16 (lower), reasonably spherical particle aggregates of approximately 150 nm in diameter partially fuse together without any directional order.

4.2. Emulsions stabilised by single particle type

Following the discovery of the interesting microstructures of the phases observed in Section 4.1, a wide range of both o/w and w/o emulsions stabilised by either hydrophilic or hydrophobic silica particles respectively with oils of different volatility were left in open vessels until both liquid phases had evaporated completely. SEM images were then obtained for the dry solid residues [34]. Fig. 17 gives representative images of some of the systems. For 10 vol.% o/w emulsions of methylcyclohexane at low (upper) and high (middle) particle concentration, a sponge-like structure is seen similar to that of certain cheeses. Comparison of the average cavity size with the drop diameters of the precursor emulsions shows that there is a close correlation between the two, suggesting that the cavity results from loss of the oil component. The characteristic size within the residue can thus be tuned by adjusting the drop size in the original emulsion (either by changing the particle concentration as here

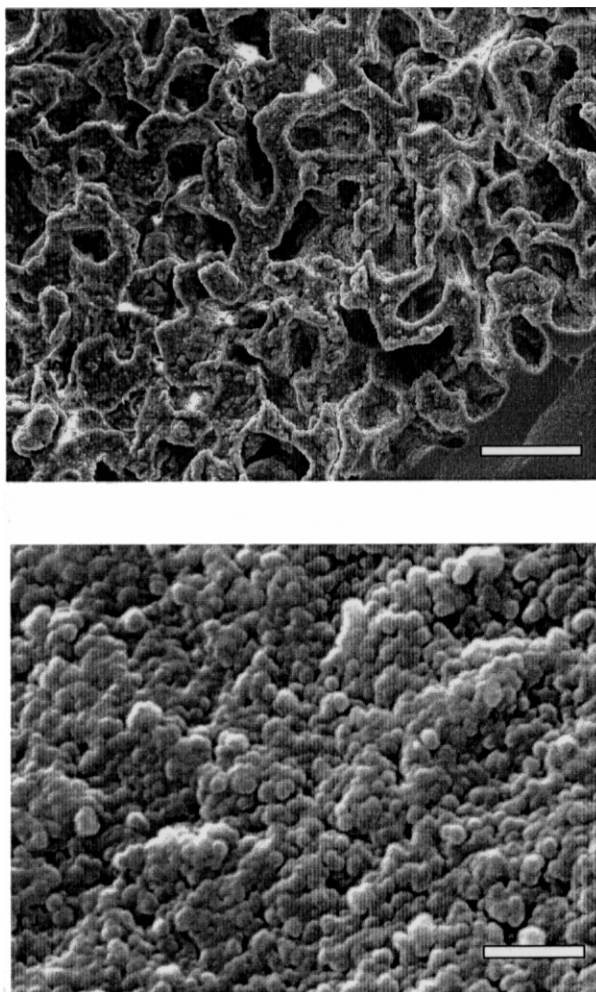


Fig. 16. SEM images of solid phase left after evaporation of toluene and water from an emulsion ($\phi_w = 0.5$) stabilised by a mixture of hydrophilic and hydrophobic silica particles: (upper) 1.25 wt.% hydrophobic + 1.25 wt.% hydrophilic particles, w/o emulsion. Scale bar corresponds to 100 μm . (lower) 1.0 wt.% hydrophobic + 3.8 wt.% hydrophilic particles, o/w emulsion. Scale bar corresponds to 1 μm . Taken from ref. [32].

or by changing the oil volume fraction). A similar cavity structure is formed after loss of water from a w/o emulsion of hexane (Fig. 17, lower) but the cavity shape is less well defined. In other systems (not shown), the residues are of a different structure completely in which it appears that the inner spherical cavity surfaces are not exposed. Elucidation of the factors determining which morphology is obtained,

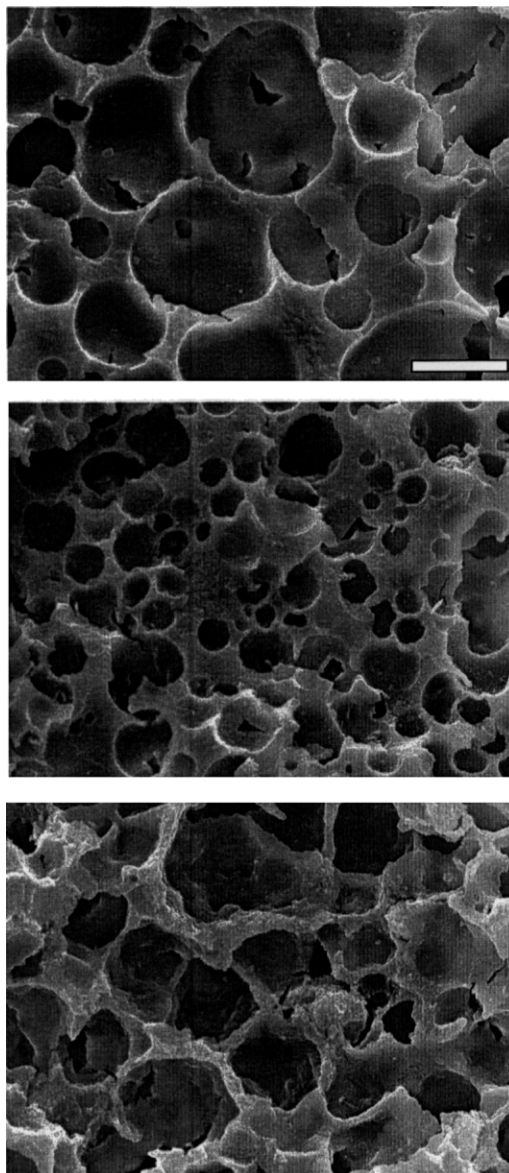


Fig. 17. SEM images of solid phases left after evaporation of oil and water from silica-stabilised emulsions: (upper) 10% methylcyclohexane-in-water with 1 wt.% hydrophilic silica; (middle) 10% methylcyclohexane-in-water with 4 wt.% hydrophilic silica; (lower) 10% water-in-hexane with 4 wt.% hydrophobic silica. Scale bar corresponds to 20 μm in all cases. Taken from ref. [34].

viz. sponge-like or less porous, awaits the completion of the systematic series of samples currently underway.

5. Some aspects of the origins of stability of solid-stabilised emulsions

There are a number of factors that appear to govern the stability of particle-stabilised emulsions. For example it is known that for high stability, contact angles, θ_{ow} of particles with the oil/water interfaces should not be too remote from 90° , and that particle roughness (and associated contact angle hysteresis) is beneficial for stability [53]. Usually, for oil and water volume fractions of approximately 0.5, particles with $\theta_{ow} < 90^\circ$ favour the formation of o/w emulsions whilst w/o emulsions result for $\theta_{ow} > 90^\circ$. However, as seen earlier, changing the volume fractions of oil and water can lead to emulsion inversion. Denkov et al. [54] have proposed a possible role of particles, bridging a thin emulsion film between two approaching drops, in stabilisation of the film. Menon et al. [55–59], and more recently Levine et al. [4,60–63], have considered in some detail the free energy changes that accompany the formation of emulsion drops coated by close-packed monodisperse spherical particles. Other relevant work is also reported by, for example, Jaques et al. [64] and Niven et al. [65]. It has to be said, however, that theory developed to date leaves unexplained much of the growing corpus of detailed experimental findings.

Recently, we have built on the work of Levine et al. to include the possible influence of line tension and of monolayer curvature energies on emulsion stability and preferred emulsion type [66,67]. Here we introduce some of the theoretical work of Levine and co-workers and some of our recent extensions to this work.

5.1. Free energy of drop formation

The free energy of (monodisperse) emulsion formation, $\Delta_{emul}G$, is given by the product of the free energy of formation of a particle-coated drop, $\Delta_{drop}G$, and the number of drops in the emulsion, n_d . It is assumed here that drop formation is effected by adsorption of n_p particles from the *continuous* (more wetting) bulk phase to form a hexagonally close-packed (HCP) monolayer around the drop. Drop formation can be achieved, conceptually, by first forming an uncoated liquid drop, radius R , and then by allowing n_p particles to adsorb at the drop surface. Adsorption results in swelling of the drop by an amount dependent on the particle radius, r , and the contact angle θ_{ow} . With reference to Fig. 18 there are two radii of interest for the particle-coated drop; these are the radius, R_{ll} , up to the spherically curved liquid–liquid interface and the radius, R_{pc} , up to the spherically curved interface defined by particle–particle contacts. The adsorption free energy of a particle to a spherically curved oil–water interface depends on the radius of the drop, R_{ll} , which can be obtained from R , r and θ_{ow} . Levine and Bowen [61] give the ratio $(R_{ll}/R)^3$

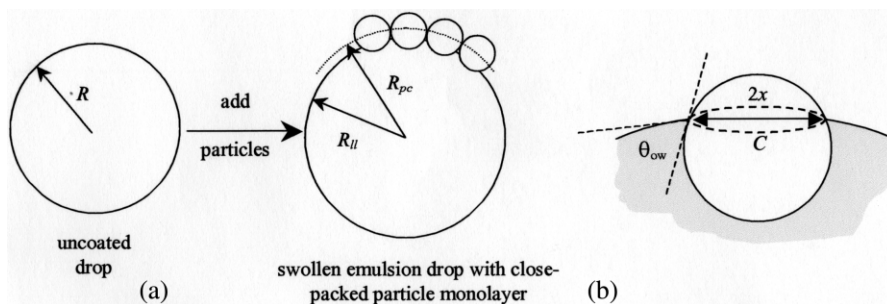


Fig. 18. (a) Definition of relevant drop radii in emulsion formation. (b) A spherical particle resting in a drop interface, showing the contact angle θ_{ow} and circular contact line C with radius x .

as the truncated series

$$\left(\frac{R_{II}}{R}\right)^3 = 1 + (r/4R)n_p(r/R)^2[(2 + \cos\theta_{ow})(1 - \cos\theta_{ow})^2 - (9r/4R)\sin^4\theta_{ow} + \dots] \quad (3)$$

The expression for the free energy of adsorption of a single particle (with $\theta_{ow} < 90^\circ$) onto the curved droplet interface, $\Delta_{int}G$, was also given as a truncated series:

$$\Delta_{int}G = \pi r^2 \gamma_{ow} (1 - \cos\theta_{ow})^2 \left\{ 1 - 2r(2 + \cos\theta_{ow})/(3R) + (3/4)[r(1 + \cos\theta_{ow})/R]^2 + \dots \right\} \quad (4)$$

where γ_{ow} is the interfacial tension of the oil–water interface. For a plane liquid interface ($r/R=0$), and the well-known equation results (for $\theta_{ow} < 90^\circ$)

$$\Delta_{int}G = -\pi r^2 \gamma_{ow} (1 - \cos\theta_{ow})^2 \quad (5)$$

In Eq. (5), which is the equivalent of Eq. (2) for $\theta_{ow} < 90^\circ$, the subscript ‘int’ signifies that the free energy change results from changes in interfacial areas (and, later, the creation of 3-phase contact lines) that accompany adsorption; the entropy of adsorption is not included at this stage (see later).

Our own approach [66,67] has led to an explicit expression for the adsorption free energy of a spherical particle on a spherically curved drop interface

$$\Delta_{int}G = 2\pi \gamma_{ow} [r^2(1 \pm \cos\alpha)\cos\theta_{ow} - R_{II}^2(1 - \cos\beta)] \quad (6)$$

in which $\alpha = \sin^{-1}(x/r)$ and $\beta = \sin^{-1}(x/R_{II})$, x being the radius of the 3-phase contact line around the particle at the interface (Fig. 18b). The $-$ and $+$ signs in brackets are to be taken, respectively, for $\theta_{ow} < 90^\circ$ and $\theta_{ow} > 90^\circ$. Values of $\Delta_{int}G$ given by Eq. (4) and Eq. (6) are in close mutual agreement.

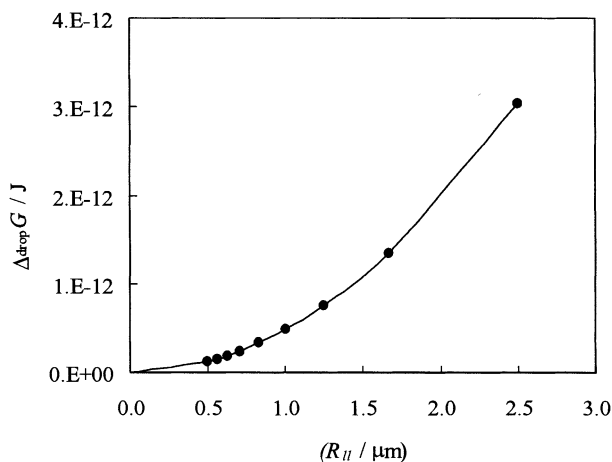


Fig. 19. Free energy change accompanying the formation of emulsion drops, radii R_{II} , coated with HCP monolayers of particles, radius $r=10$ nm and contact angle $\theta_{ow}=60^\circ$. The oil–water interfacial tension $\gamma_{ow}=50$ mN m $^{-1}$. Points are calculated using the treatment of Levine and Bowen [61] and the full line is obtained from our own work [66,67].

Neglecting for the moment the entropy change on particle adsorption (other than that associated with surface area changes), the free energy of drop formation, $\Delta_{\text{drop}}G$, can be obtained from the free energy of forming an uncovered drop, radius R , the free energy of swelling the drop to radius R_{II} and then the free energy, $n_p\Delta_{\text{int}}G$, of adsorbing n_p particles at the drop interface (without further swelling) from the continuous phase. Some values of $\Delta_{\text{drop}}G$ so obtained are given in Fig. 19 as a function of the drop radius R_{II} . The values are always positive and become more so with increasing drop size. There is excellent agreement between our own values and those obtained using the equations of Levine and Bowen [61].

We have estimated the free energy change arising from the entropy of adsorption as follows. Overbeek et al. [68] give an expression for the mixing free energy, $n_p\Delta_{\text{mix}}G = -n_p\Delta_{\text{demix}}G$, of n_p hard spheres with a liquid (continuous phase) from an initially hexagonally close-packed 3-dimensional array in the liquid. If the entropy change in taking particles from a 3-dimensional to a 2-dimensional HCP state is neglected, the component of the adsorption free energy due to the entropy of adsorption is $n_pT\Delta_{\text{demix}}S$ where $\Delta_{\text{demix}}S$ is the entropy of demixing the particles from a dispersion to form a 3-dimensional HCP array in the continuous phase. Thus, from Overbeek et al.,

$$n_pT\Delta_{\text{demix}}S = n_pT\Delta_{\text{ads}}S = -n_p\Delta_{\text{demix}}G = n_p kT \left(\ln\phi + \phi \frac{4-3\phi}{(1-\phi)^2} - 19.25 \right) \quad (7)$$

where ϕ is the volume fraction of the n_p particles in the continuous phase.

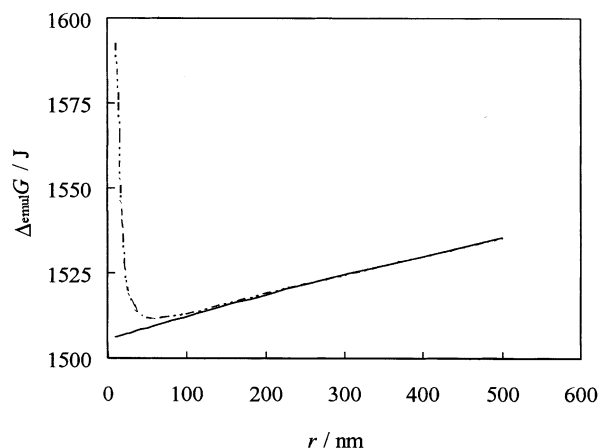


Fig. 20. Effect of particle radius r on the free energy of emulsion formation, $\Delta_{\text{emul}}G$. The dashed and full curves are, respectively, for calculations that include or exclude the entropy of adsorption. The o/w emulsion consists of 0.5 m^3 each of oil and water, with interfacial tension 10 mN m^{-1} ; the contact angle of the particles with the oil–water interface is taken as 75° and the un-swollen drop radius R is $5 \text{ }\mu\text{m}$ in all cases.

The entropy of adsorption, $n_p \Delta_{\text{ads}} S$ is negative so the contribution to $\Delta_{\text{drop}} G$ is positive. As the particle radius falls, the number of particles needed to cover a drop with a given radius rises and $n_p T \Delta_{\text{ads}} S$ becomes more positive. An example of the way in which particle radius affects $\Delta_{\text{emul}} G (=n_d \Delta_{\text{drop}} G)$ through the entropy of adsorption is given in Fig. 20. The dashed curve is for calculations that include the entropy and the full curve results when no such account is taken. Significantly, inclusion of the entropy term leads to a minimum in $\Delta_{\text{emul}} G$ implying that, for a given particle size, there is a ‘favoured’ drop size in the emulsion. Of course, it may well be that such a favoured size is not attained in practice.

Levine and Bowen [63] have considered various types of lateral interactions between adsorbed particles, and point out that if equilibrium adsorption were to be achieved, so that the chemical potential of an adsorbed and a dispersed particle would be equal, the strongly negative adsorption energy $\Delta_{\text{int}} G$ must be just offset by lateral repulsions between adsorbed particles. They concluded that normal ‘colloid forces’ could not provide such repulsion and that in general adsorption equilibrium is not achieved. Inclusion of a repulsive energy between particles will obviously render $\Delta_{\text{int}} G$, etc., more positive.

It is clear from the foregoing that, for the systems envisaged so far, solid-stabilised emulsions will not be thermodynamically stable, as was appreciated by e.g. Tadros and Vincent [53]. However, as detailed earlier, small ‘nanoparticles’ can be very effective indeed in stabilising emulsions. This raises the possibility that in some circumstances line tension might be an important parameter in determining emulsion stability; the smaller the particles stabilising drops the greater the total length of the three phase contact line that is formed when a drop of given radius is

produced. As will be seen, under these circumstances a small positive line tension could exclude particles from drop interfaces and a small negative line tension could result in a negative free energy of emulsion formation. Positive line tension can also produce energy barriers to particle adsorption and desorption at drop interfaces and can therefore, in principle at least, affect the kinetics of emulsion breakdown. The kinetics of breakdown, and hence preferred emulsion type, can also be influenced by the existence and operation of curvature energies of close-packed particle monolayers just as in surfactant-stabilised emulsions. In what follows we consider the possible importance of line tension and of monolayer curvature energy on the stability and preferred type of solid-stabilised emulsions.

5.2. Effects of line tension

Line tension, τ , arises as a result of the excess free energy (positive or negative) associated with a unit length of a 3-phase contact line [69], in the present case that skirting a particle resting in an oil–water interface. The units of τ are those of force (i.e. energy per unit length) and line tension is a one-dimensional analogue of surface tension, although surface tension can only be positive (i.e. contractile). The origins of line tension lie in the surface forces that operate between the oil–water interface and the solid surface in the vicinity of the contact region (see e.g. ref. [70]). The magnitude of τ is expected to be of the order of the product of an interfacial tension and a molecular dimension, centred on say 10^{-11} N.³ Both positive and negative line tensions have, however, been reported which exceed this by 5 orders of magnitude or more [73]. We will assume here that realistic magnitudes are between approximately 10^{-11} N and 10^{-10} N. As will be appreciated later, values of say $+$ and -10^{-6} N would have quite drastic effects on the stabilisation of emulsions by particles with radii in the region of 10–20 nm. It has to be said that the measurement of τ is usually somewhat ambiguous [74,75] and, in general, values and signs of τ will be uncertain for specific systems, and it is certainly not possible at present to design systems exhibiting required values and signs of line tension.

If the effects of line tension are taken into account, Eq. (6) for $\Delta_{\text{int}}G$ becomes [67]

$$\Delta_{\text{int}}G = 2\pi\gamma_{\text{ow}} \left[r^2(1 \pm \cos\alpha)\cos\theta_{\text{ow}} \left(1 - \frac{\tau\cos\beta}{\gamma_{\text{ow}}x} \right) - R_{\text{II}}^2(1 - \cos\beta) \right] + 2\pi x\tau \quad (8)$$

where, as in Eq. (6), the $-$ and $+$ signs in brackets are to be taken, respectively, for $\theta < 90^\circ$ and $\theta > 90^\circ$. There are several potential consequences of the operation of line tension, depending on the magnitude and sign of τ , the particle radius and

³ We note that line tension can depend upon the curvature of the contact line [71]. It is also related to the contact angle and to the interfacial tensions in the system. For example, based on a simple model, Marmur [72] gives the expression (in our nomenclature): $\tau = 4\delta\sqrt{\gamma_{\text{so}}\gamma_{\text{ow}}}\cos\theta_{\text{ow}}$. δ is a typical molecular ‘diameter’ and γ_{so} and γ_{ow} are tensions of the solid–oil and oil–water interfaces, respectively.

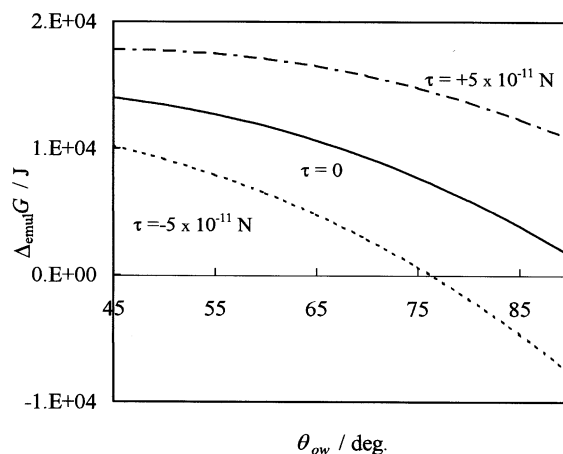


Fig. 21. Free energy of formation of 1 m^3 of o/w emulsion, containing equal volumes of oil and water, as a function of contact angle θ_{ow} . Parameters used are: un-swollen drop radius $R=1 \text{ }\mu\text{m}$, $r=15 \text{ nm}$ and $\gamma_{ow}=10 \text{ mN m}^{-1}$. The full line is for $\tau=0$, the upper line is for $\tau=+5 \times 10^{-11} \text{ N}$ and for the lower line $\tau=-5 \times 10^{-11} \text{ N}$. The free energy in the latter case becomes negative for θ_{ow} above approximately 76° . For $\theta_{ow} > 90^\circ$ we note that the curves are mirrored about 90° . For angles less than approximately 45° , the line tension $\tau=+5 \times 10^{-11} \text{ N}$ exceeds the maximum line tension τ_m and there is no stable equilibrium for particles in the interface (see text).

wettability (θ_{ow}) and the oil/water interfacial tension γ_{ow} . If τ is negative and the stabilising particles are small enough, the free energy of droplet (and emulsion) formation can become negative in certain regimes of particle wettability. Conversely, for sufficiently large positive τ , $\Delta_{int}G$ can become positive so that particle adsorption (and therefore emulsion stabilisation) is no longer thermodynamically feasible.

In Fig. 21 the free energy of emulsion formation, $\Delta_{emul}G$, is shown as a function of contact angle for $\theta_{ow} < 90^\circ$; the curves, however, are mirrored about 90° . In the example shown, the droplet radius R (prior to particle adsorption) $= 1 \text{ }\mu\text{m}$, $r=15 \text{ nm}$, $\gamma_{ow}=10 \text{ mN m}^{-1}$ and the effects of $\tau=+5 \times 10^{-11} \text{ N}$ and $-5 \times 10^{-11} \text{ N}$ are illustrated. (N.B. As discussed in the footnote, τ and θ_{ow} are related via interfacial tensions. We have chosen particular values of τ here for all θ_{ow} , and γ_{so} will of course vary along the curves). It is seen, for the case of negative τ , that for $\theta_{ow} > 76^\circ$ (and $< 104^\circ$) $\Delta_{emul}G$ is negative, suggesting the possibility that if small negative line tensions exist (in the absence of strong inter-particle repulsion), solid-stabilised emulsions could be thermodynamically stable. Perhaps more importantly, relatively small positive line tensions can inhibit particle adsorption, either by rendering $\Delta_{int}G$ positive or by creating an energy barrier to adsorption. These possibilities are discussed below; for simplicity the ideas are introduced by reference to planar liquid interfaces. In the context, this is reasonable for systems with nanometer sized-particles since the ratio of drop to particle radius will usually be large so that curvature effects are expected to be small.

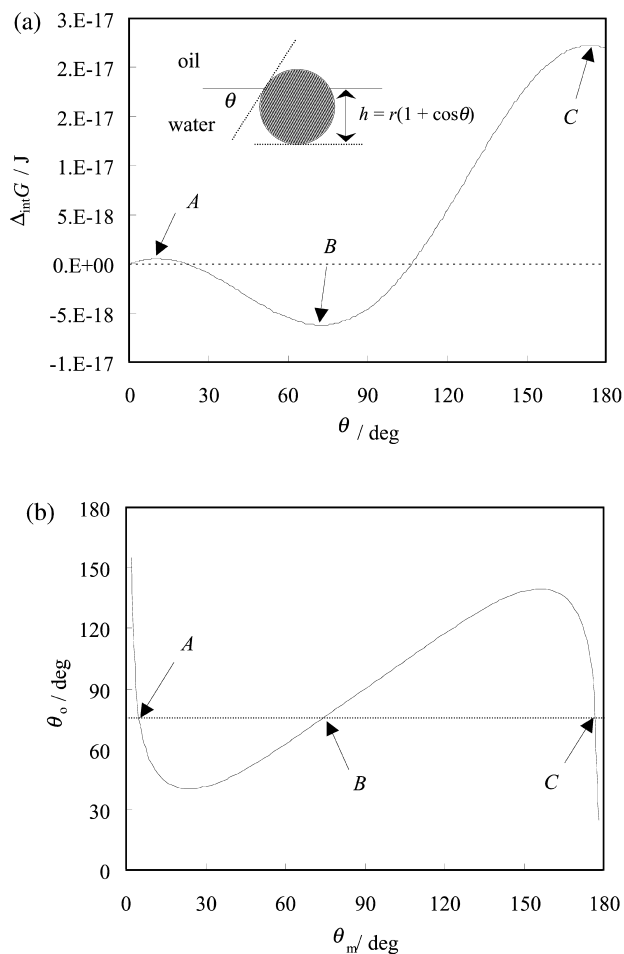


Fig. 22. (a) The variation of $\Delta_{\text{int}}G$ with θ_{ow} as a spherical particle is pushed through a plane liquid interface. The parameters assumed are: $r=15$ nm, $\gamma_{\text{ow}}=30$ mN m $^{-1}$, $\theta_o=75^\circ$ and $\tau=6\times 10^{-11}$ N. The curve exhibits 2 maxima (at points A and C) and one minimum (at point B). (b) For a given θ_o there are, according to Eq. (10), 3 values of θ_m . Two (denoted by A and C) correspond to maximum values of energy and one to a minimum value. Parameters are the same as in (a) and points A, B and C correspond to those similarly denoted in (a).

Suppose a spherical particle is pushed vertically through a liquid interface that remains planar up to the contact line. The free energy of the system varies with the depth of particle immersion, h , which is related to θ_{ow} and r by $h=r(1+\cos\theta_{\text{ow}})$. For a planar liquid interface $\Delta_{\text{int}}G$ is given by [76]

$$\Delta_{\text{int}}G = \pi r^2 \gamma_{\text{ow}} [2\cos\theta_o(1 - \cos\theta_{\text{ow}}) - \sin^2\theta_{\text{ow}}] + 2\pi r \tau \sin\theta_{\text{ow}} \quad (9)$$

where θ_o is the equilibrium contact angle in the absence of the influence of line

tension. It is the contact angle that would usually be measured experimentally, using a macroscopic drop resting on a flat plate. An example of the variation of $\Delta_{\text{int}}G$ with θ_{ow} (hence h) is illustrated in Fig. 22a for a system with positive τ ; it is seen that $\Delta_{\text{int}}G$ has 2 maximum values (at points A and C in the figure) and one minimum value (at point B). The minimum corresponds to the equilibrium position of the particle in the interface. Taking the derivative of $\Delta_{\text{int}}G$ with respect to θ_{ow} and setting the result equal to zero gives the relationship between θ_o and the contact angles θ_m at the maxima and the minimum

$$\cos\theta_o = \cos\theta_m \left(1 - \frac{\tau}{\gamma_{\text{ow}} r \sin\theta_m} \right) \quad (10)$$

A plot of θ_o vs. θ_m in Fig. 22b illustrates that for a given θ_o there are 3 values of θ_m , at the points A, B and C, which correspond to the similarly designated points in Fig. 22a.

With reference to Fig. 22a, as the positive line tension is increased the curve moves to higher energies and at some stage, when $\tau = \tau_c$, the energy minimum (point B) occurs at $\Delta_{\text{int}}G = 0$. On further increasing τ , at some value τ_{max} , point B becomes a point of inflexion. For line tensions between τ_c and τ_{max} minima do exist at points B, but $\Delta_{\text{int}}G$ values at the minima are greater than zero and points B correspond to metastable configurations of the particle in the interface. For $\tau > \tau_{\text{max}}$ however, no stable or metastable configurations are possible and particle adsorption and emulsion stabilisation cannot occur. The maximum line tension τ_{max} is related to θ_o by the simple expression [76]

$$\tau_{\text{max}} = \gamma_{\text{ow}} r [1 - (\cos\theta_o)^{2/3}]^{3/2} \quad (11)$$

and for the system represented in Fig. 22, $\tau_{\text{max}} = 2.3 \times 10^{-10}$ N. For the same system, the value of τ_c , calculated as explained in ref. [76] is 1.4×10^{-10} N. It is worth noting that Mingins and Scheludko [74] report an experimental value of τ of $+1 \times 10^{-10}$ N for small spherical glass beads resting at an air–water interface. As θ_o or r falls so, according to Eq. (11), does τ_{max} . If, in the system considered in Fig. 22a, θ_o is reduced from 75 to 45° for example, τ_{max} becomes $+7.7 \times 10^{-11}$ N, so that if τ were 1×10^{-10} N, particles with radius 15 nm could not adsorb at drop interfaces.

In summary then, effects resulting from positive line tension become more important as particle size is reduced and as θ_o is shifted further from 90° . It is quite possible in principle that small positive line tensions could prevent nanometer-sized spherical particles from adsorbing at oil–water interfaces. Experimentally, it is recognised that particles exhibiting rather high or low contact angles relative to 90° are ineffective emulsion stabilisers [23].

Even if positive τ does not render $\Delta_{\text{int}}G$ positive, it does result in the formation of an energy barrier to adsorption, as seen in Fig. 22a. For particle adsorption from the more wetting phase, e.g. water for $\theta_{\text{ow}} < 90^\circ$, the value of $\Delta_{\text{int}}G$ at the maximum

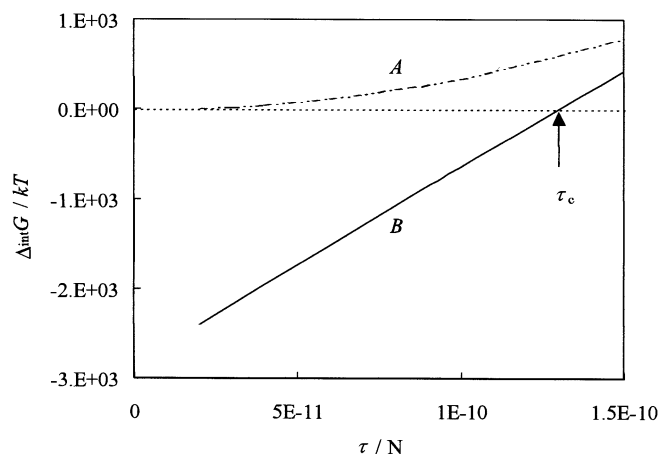


Fig. 23. Maximum and minimum free energies, in units of kT , as a function of line tension for a particle ($r = 15$ nm) being pushed through a plane oil–water interface (tension 30 mN m^{-1}); θ_o is taken as 75° . Curve A represents the lower of the two energy maxima, i.e. the energy barrier to adsorption from the more wetting bulk phase (water). For the lowest value of τ represented, 2×10^{-11} N, the energy barrier is approximately $14 kT$ and for the highest τ (1.5×10^{-10} N) the barrier is approximately $790 kT$. Curve B represents energy minima, i.e. free energies of adsorption to equilibrium positions in the interface; for zero free energy $\tau = \tau_c$.

point A in Fig. 22a constitutes the energy barrier to adsorption from water. It can be calculated as a function of τ (for given θ_o , r and γ_{ow}) by use of Eq. (9) with $\theta_{ow} = \theta_m$. The value of θ_m is obtained from Eq. (10). The energy barrier to adsorption from the continuous phase is shown in Fig. 23, in units of kT , as a function of line tension. For the lowest value of τ represented (2×10^{-11} N) the energy barrier is approximately $14 kT$, and for $\tau = 1.5 \times 10^{-10}$ N it is $790 kT$. It can be appreciated therefore that, if the particles are small enough, very small values of positive τ can result in barriers sufficiently large to inhibit adsorption and hence preclude emulsion stabilisation.

5.3. Curvature properties of close-packed particle monolayers

Emulsions stabilised by surfactants are not thermodynamically stable, but there are various possible energy barriers acting against flocculation and coalescence, which give rise to ‘kinetic’ stability of emulsions. Kabalnov and Wennerström [77] have shown that an energy barrier to coalescence of two drops can arise as a result of the effect of curvature properties of the surfactant layers on the growth of a neck joining two drops. There is no barrier in systems where the spontaneous curvature of the monolayers is toward the continuous phase, (i.e. in ‘unnatural’ emulsions) but a barrier does exist if the spontaneous curvature is towards the droplet (as is the case for the ‘preferred’ emulsion type). The question naturally arises whether

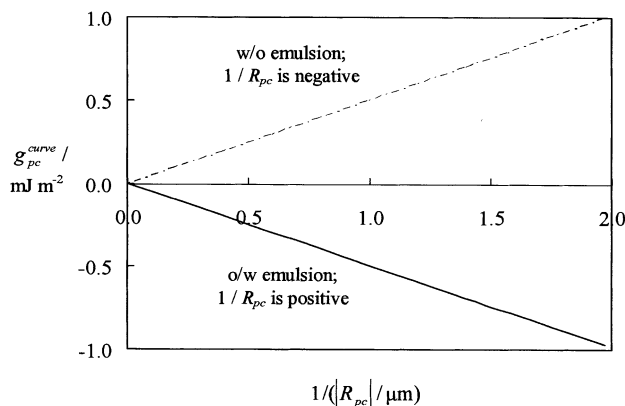


Fig. 24. Curvature energy as a function of the magnitude of drop curvature, $1/|R_{pc}|$. The parameters used are: $\gamma_{ow} = 50 \text{ mN m}^{-1}$, $\theta_{ow} = 60^\circ$ and $r = 10 \text{ nm}$. The preferred emulsion type is o/w for which the curvature is positive and the curvature energy is negative. For w/o emulsions the curvature energy is positive and the curvature is negative.

such monolayer curvature properties exist for close-packed particle monolayers. As seen earlier, there is a preferred emulsion type that is related to particle wettability, and one could regard wettability as being parallel to the hydrophile–lipophile balance (HLB) in surfactant systems [2].

We seek here to calculate the free energy change when a unit area of plane close-packed particle monolayer at an oil–water interface is bent to a spherically curved state with specified radius. Since the monolayer has finite thickness, the radius on the ‘inside’ of the monolayer differs from that on the ‘outside’ when the film is curved. There is a *neutral* plane (see e.g. ref. [78]) through the monolayer such that the number of particles in unit area is independent of the film curvature. It turns out that the number of particles in the spherically curved interface defined by particle–particle contacts, with radius R_{pc} , is almost independent of drop curvature, and this is taken here to be the neutral plane.

The free energy of emulsion formation can be calculated as a function of drop radius as described above; the free energy, g_{pc} , of forming unit area of emulsion drop interface (defined by R_{pc}) is then readily obtained. This free energy becomes less positive the higher the value of the curvature of the ‘preferred’ emulsion type (taken as positive), and conversely more positive the higher the negative curvature. The curvature free energy g_{pc}^{curve} is the value of g_{pc} for a curved drop interface less the corresponding value for a plane interface. The effect of the magnitude of curvature on g_{pc}^{curve} is illustrated in Fig. 24 for systems with the parameters indicated in the legend. The particle contact angle chosen is less than 90° so that the preferred emulsion type is o/w, and the radius of curvature in this case is positive. The curvature free energies of surfaces of w/o drops (which have negative curvature) are positive.

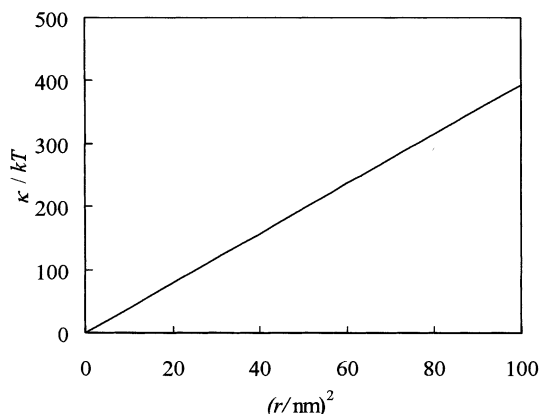


Fig. 25. Linear variation of κ with r^2 for $\theta_{ow} = 60^\circ$ and $\gamma_{ow} = 50 \text{ mN m}^{-1}$.

The variation of g_{pc} with drop curvature can be discussed in terms of the Helfrich approach [79], which leads to the quadratic expression for g_{pc} in terms of $1/R_{pc}$

$$g_{pc} = \left(\frac{2\kappa}{R_o^2} + \gamma^* \right) - \frac{4\kappa}{R_o} \frac{1}{R_{pc}} + (2\kappa + \bar{\kappa}) \frac{1}{R_{pc}^2} \quad (12)$$

In Eq. (12) κ and $\bar{\kappa}$ are bending elastic moduli (having units of energy), $\bar{\kappa}$ being the saddle-splay modulus that takes account of saddle-like deformations of the interface. The tension γ^* is an effective tension of the plane particle-coated interface, and its significance has been discussed (in a different context) by Menon et al. [56] and by Levine and Bowen [63]. The quantity R_o is a spontaneous drop radius corresponding to a minimum in g_{pc} . Our model does not yield a spontaneous radius, as could be anticipated from Fig. 24. As drop size is reduced, at some stage the assumption of hexagonal close-packing will become untenable. It may well be that if this (rather complex) effect were to be taken into account a minimum in energy would be observed.

It is evident from Eq. (12) that values of $(2\kappa + \bar{\kappa})$ can be obtained from quadratic fits of g_{pc} as a function of $1/R_{pc}$. It is found that such fits are extremely good and, ignoring $\bar{\kappa}$ (which is negative and of smaller magnitude than κ), it is possible to obtain reasonable estimates of κ as a function of the various relevant quantities. The dependence of κ on γ_{ow} , θ_{ow} and τ will be reported on elsewhere [66]. Here, to conclude, it is simply shown how calculated values of κ depend on particle radius. Values of κ/kT are plotted in Fig. 25 as a function of r^2 for systems in which $\gamma_{ow} = 50 \text{ mN m}^{-1}$ and $\theta_{ow} = 60^\circ$. It is seen that the plot is rectilinear; the data are closely fitted by

$$\frac{\kappa}{kT} = 3.9(r/\text{nm})^2 \quad (13)$$

To get an indication of how similar, or otherwise, the curvature properties of particle and surfactant monolayers are, values of κ in systems containing very small particles, with size similar to that of simple low molar mass surfactant molecules, have been calculated. As an example, for systems described by Eq. (13) with $r=0.5$ nm the value of κ/kT is approximately 1, which is reassuringly close to values of 0.4–1.1 quoted in ref. [80] for monolayers of a range of simple ionic surfactants at oil–water interfaces.

6. Summary and conclusions

Solid particles adsorb strongly at the oil–water interface and are able to stabilise emulsions of oil and water. The key parameter is the contact angle (θ_{ow}) made by the oil–water interface on the surface of the particle. For θ_{ow} not too far from 90° the energy required to remove even nanoparticles from this interface can be several thousand times kT and hence the adsorption can be considered irreversible. Particles for which $\theta_{ow} < 90^\circ$ tend to stabilise oil-in-water (o/w) emulsions whereas those with $\theta_{ow} > 90^\circ$ stabilise water-in-oil (w/o) emulsions. Stable multiple emulsions of w/o/w and o/w/o can be made using suitable combinations of particle types.

Unlike emulsions stabilised by a single surfactant type, those made with small particles can be inverted from w/o to o/w simply by increasing the volume fraction ϕ_w of water. For surfactant systems this behaviour occurs only when a combination of surfactants is used. Emulsions stabilised by particles are most stable near to this inversion point, in complete contrast to those made using surfactants where these tend to be the least stable. The value of ϕ_w needed for phase inversion depends on the particle wettability and on the type of the oil, especially any polar nature. Both of these effects have been accounted for by predicting contact angles from dispersion and polar components of the solid surface free energy and the corresponding components of the surface tension of the oil. Freeze fracture SEM images show that in most emulsions the oil–water interface is completely covered with a layer of particles. There is evidence that in some systems weak flocculation of the particles improves the emulsion stability.

Interesting porous solids are produced when both the oil and water phases are allowed to evaporate from particle-stabilised emulsions. Emulsions stabilised by a mixture of particle types and close to inversion leave a bicontinuous structure reminiscent of those seen in third phase microemulsions. The residues from emulsions made with a single particle type are more reminiscent of the parent emulsions, especially these of o/w, for which the cavities have sizes close to those of the original oil droplet size distribution.

We have shown that the operation of small line tensions can in principle cause significant effects on emulsion stability. The influence depends on particle radius, as expected, being greater the smaller the particles. Relatively small positive line tension can (a) result in positive free energies of particle adsorption, particularly for contact angles remote from 90° , and (b) create activation barriers to adsorption even though the free energy of adsorption may be negative. Negative line tension can lead to negative free energies of emulsion formation, particularly for angles not

far removed from 90°. Close-packed particle monolayers appear to have curvature properties similar in type to those of surfactant monolayers. For example, for particles with size comparable to a typical low molar mass surfactant molecule, the bending elastic modulus, κ , of a monolayer is similar in magnitude to that for surfactant monolayers (around kT). This means that ideas developed (by Kabalnov and Wennerström) for the stability and type of surfactant-stabilised emulsions could also be applied to solid-stabilised emulsions.

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