De-gassed water and surfactant-free emulsions: History, controversy, and possible applications

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Abstract

Recent reports claiming stabilisation of surfactant-free oil-in-water emulsions (o/w SFEM's) have intrigued the colloid science community, and been reported in both the scientific literature and popular press. Key to the formation of SFEM's is a sequence of solidification by freeze quenching, degassing by action of vacuum, then thawing, known as freeze-pump-thaw (F-P-T). It is believed that the "emulsification" is caused by a reduction of hydrophobic interactions owing removal of dissolved gas after these F-P-T cycles. This review summarises literature on SFEM's, covering experiments, proposed mechanisms, and some potentially exciting applications.
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1. Introduction

It is not often that physical chemistry research headlines in the world's newspapers. However, there was a flurry popular press reports [1–7] triggered by a paper published a group at Australian National University (ANU), led by Richard Pashley. The group claimed de-gassed water is "a better cleaning agent" than a normal detergent solution [8]. This surprising finding, that water treated by de-gassing can sustain stable oil droplet dispersions, raised many questions about the nature of colloids and the interactions between constituents in an oil–water emulsion. It is known that common hydrocarbon oils may be weakly soluble, or totally insoluble in water, depending on the

chemical nature of the oil and temperature. To affect dissolution of a solute, strongly hydrogen bonded water molecules have to be separated. The work done in reorganization of water internal structure is normally offset by stronger solvent-solute bonding. Hydrophobic species such as oil lack these favourable interactions with water molecules and are thus essentially insoluble.

Generally, emulsions of oil and water can only be generated by addition of a third component, typically surfactants, polymers or certain surface treated particles (Pickering or Ramsden emulsions). These additives stabilise colloidal oil droplets, preventing coagulation, coalescence and phase separation from the aqueous dispersion medium. Emulsion stability is governed by interactions between the dispersed particles, normally explained within the framework of Derjaguin–Landau–Verwey–Overbeek (DLVO) theory. This DLVO approach considers a balance of the main two forces: destabilising inter-droplet van der Waals

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attractions, and repulsive electrostatic forces, which serve to stabilise the dispersion. The total potential, V_T, under the limiting conditions of (a) low interparticle separations h compared to the particle diameter $2a$ (i.e. $h \ll 2a$), and (b) particle radius below three times the Debye length (i.e. $a < 3\kappa^{-1}$), is concisely expressed by Eq. (1) [9]:

$$V_T = \frac{a}{kT}\left[2\pi\varepsilon\psi_\delta^2\exp(-\kappa h) - \frac{A}{12h}\right] \quad (1)$$

In Eq. (1) ε is solvent permittivity, ψ_δ is a surface potential and A is a Hamaker constant for the system. The total potential is given in comparison to thermal energy kT.

Consider the possibility of surfactant-free free oil-in-water emulsions (o/w SFEM's). Obviously, without any stabilising adsorbed monolayers (surfactants, polymers or particles), *steric* stabilising repulsions are absent. Therefore the stabilising interactions must be *electrostatic* in origin, consistent with DLVO theory. Then, in a system comprising only oil and water, what would be the source of the necessary electrostatic surface potentials? In the first ANU paper on o/w SFEM's [10] it was shown that DLVO theory would predict stabilisation of dispersed dodecane oil droplets in water if hydroxyl ions adsorbed on the oil–water interfaces [11,12], thereby providing a repulsive barrier to coagulation. It is proposed that these OH⁻ ions are generated by autolysis of water. Back-of-the-envelope calculations, shown on Fig. 1 (taken from reference 10) indicate if adsorbed OH⁻ layers can generate a surface potential of −50 mV, this would result in a substantial 800 kT barrier to coagulation. This energy penalty should be sufficient stabilise surfactant- (polymer-, or particle-) free emulsions. Below (section 4) experimental evidence for the stabilisation of SFEM's is reviewed, but first the origin of inherent instability of non-degassed water–oil mixtures is discussed in terms of the hydrophobic interaction (section 2), then the effects of degassing on reducing this destabilising mechanism are introduced (section 3).

2. The hydrophobic interaction

Of course, attempts to generate surfactant-free emulsions from model oils like dodecane in normal (non-degassed) water
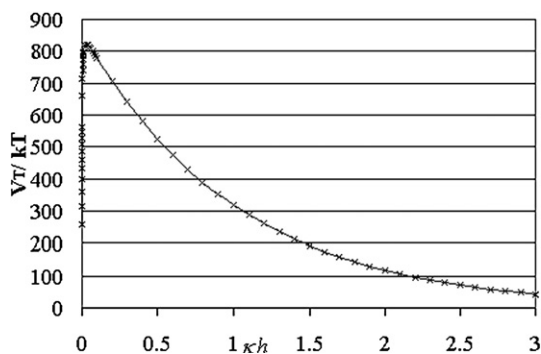

Fig. 1. DLVO potential calculated for spherical dodecane particle pairs in water. Particle radius, 0.3 μm; temperature, 298 K; Debye length, 50 nm; surface potential −50 mV, Hamaker constant 0.5×10–20 J. Dimensions suggested by Pashely. Reprinted from [10] with permission from The American Chemical Society.

are futile: the system quickly resolves into two separate liquid phases owing to the distinct absence of any *electrostatic* or *steric* stabilising interactions. There is an additional destabilising mechanism, neglected by conventional DLVO theory. Initially this "force" was dubbed a 'hydrophobic bond' [13], that was explained in terms of an entropic effect [14]: after lobbying [15], it eventually became known as the 'hydrophobic interaction'.

Unlike the name suggests, this interaction is due to water solvent properties rather than the solute [16]. The nature of this hydrophobic interaction lies in the hydrophobic effect or hydrophobic hydration, whereby water molecules try to maximise hydrogen bonding by re-orientation, as they approach a non-polar molecule [17]. This results in a tetrahedral 'iceberg-like' [18] water structure that forms around non-polar molecules (Frank and Evans took care to point out that the structure of water molecules surrounding solute molecules is not exactly like that of solid water): the extent of this solute-induced structural ordering increases with size of the non-polar solute molecules. Hence, water order increases on incorporation of non-hydrogen bonding species, decreasing system entropy so tending to be an unfavourable process. The implications are that as two dissolved oil molecules approach, water molecules must keep reorienting to maximise favourable mutual hydrogen bonding interactions.

Headway was made in the early 1980s, with the first experimental data relating the hydrophobic interaction strength to the separation of model hydrophobic surfaces [19]. This and subsequent studies [20] have tried to show the deviation of experimental interaction energies from DLVO predictions. These data suggest a longer ranging interaction (approximately 60 times greater) [21], than expected solely due to propagation of water re-orientation from a hydrophobic surface. However, even after significant and sustained efforts, consistent data are hard to come by [22]. To try to account for this long interaction range various theories have been proposed, including the effect of cavitation between hydrophobic surfaces in contact [20,21].

Any mechanism that could reduce the degree of hydrophobic interaction might eliminate attractive forces between oil molecules incorporated into water, to such an extent that hydrocarbon dispersions could become stable. The ANU team proposed that removing the dissolved gases from water cause this modification in interactions [8,10,23], then electrostatic repulsions owing to adsorbed hydroxyl ions could dominate to help stabilise long lasting emulsions.

3. Bubbles

Interfacial properties of water are known to be affected by dissolved gas [24]; dynamic surface tension [25] being an early example. Studies have suggested [21,26] changes to the hydrophobic interaction (mentioned above) arise when dissolved gases are removed from water (typically [O₂] ~ 1 mM in water at 25 °C). One explanation considers the relative stabilities of water films between hydrophobic surfaces, with and without gases [27]. After hydrophobic surfaces have come into contact with each other, vapour cavities can spontaneously form as the surfaces are separated. These vapour bridges can connect the two surfaces over long distances, as depicted Fig. 2.
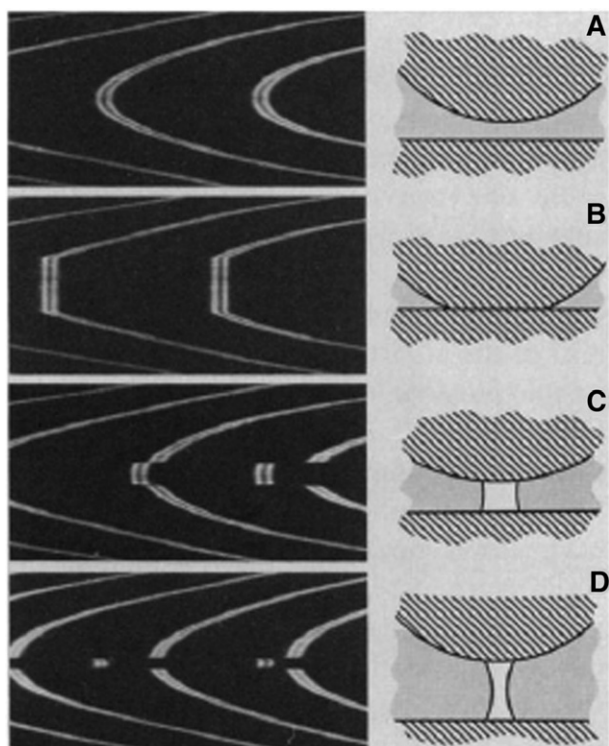
Fig. 2. The formation of vapour cavities between mica surfaces coated with dimethyldioctadecylammonium (DDOA) in water. The schematics on the right show what is inferred from the fringe patterns on the left. The patterns, obtained with a spectrometer, being caused by the difference in optical path length, which in turn was caused by the decreases in refractive index. The discontinuities in the pattern represent the vapour–water boundary. The figure shows the surfaces approaching from 100 nm (A), coming into contact (B) and separating with the vapour bridge behind them [(C) 150 nm] which decreases in diameter with separation [(D) 1 μm]. Reprinted from [27] with permission from The American Association for the Advancement of Science.

Because the interfacial free energy between the hydrophobic surface and vapour is lower than that between the surface and water, it is favourable for vapour to displace liquid water adsorbed to the surface: this leads to cavitation and hence enhanced hydrophobic interactions. If cavitation was to be prevented, for example owing to the removal of nucleation sites provided by dissolved gases, then hydrophobic interaction forces would be reduced. The importance for SFEM's is believed to be that in gas-free systems nascent emulsion oil droplets may more easily break away from the oil–water interface to generate fine dispersions, as compared to systems containing dissolved gas at the normal background levels. There are doubts, however, about whether, or not, removal of dissolved gases actually has any significant effect. Work performed with normal and de-gassed micellar surfactant solutions [28,29] shows that de-gassing changes the hydrophobic interaction by approximately 1%. It is unclear that de-gassing can be sufficiently effective to cause such significant changes in the hydrophobic interaction [30].

4. Surfactant-free emulsions

The ability of de-gassed water to sustain surfactant free hydrophobic particle dispersions had been observed [21,31,32]

long before the recent SFEM work. However, the ANU paper [10] described new methods for generating surfactant-free emulsions; the important factor is that water must be de-gassed by repeated freeze-pump-thaw (F-P-T) treatments. The hydrocarbon and water mixtures were frozen in liquid nitrogen and then repeatedly thawed under low pressure, a process that is know to remove 99.999% dissolved gas. Interestingly, it was observed that re-introduction of dissolved gas does not affect emulsion stability. The extent and stability of emulsification were assessed by absolute turbidity measurements (Fig. 3). It was proposed that removal of dissolved gas prevents cavitation (outlined in section 3), thereby facilitating break away of oil droplets from the bulk. These droplets could then absorb OH⁻ ions, hence forming electric double-layer repulsions, inducing formation of the SFEM's. Another section of the paper [10] outlined investigations of Teflon particle dispersions in normal and de-gassed waters: degassing improved stability, explained in terms of a reduction in buoyancy in the absence of gas, minimizing the tendency of particles to float and flocculate at the water surface.

Next followed a more in-depth study [23], covering effects of de-gassing with various oil–water mixtures (dodecane, squalane, hexane, octane, decane, octadecane and 4-fluorotoluene). The initial observations [10] were confirmed, and dispersed droplet sizes measured by dynamic light scattering (DLS) were presented, as well as effects of pH and added salt. The longer chain heavier, and less soluble, oils were found to form more turbid emulsions than lower molecular weight counterparts. The turbidities were found to decrease with time, but were always consistently higher than control samples made up with non-degassed water. Fig. 3 shows examples of turbidity-time traces. Squalane and octadecane droplets were observed several weeks after the F-P-T treatments. The DLS measurements showed that these emulsion droplet diameters were apparently in the micron size range, and of low polydispersity: this was explained by a fractionation process, with coalescence of small droplets and creaming of large particles; hence the remaining droplets observed by DLS were apparently "monodisperse".

The effects of added salt and changing pH were investigated for the most stable (squalane) dispersion. Lowering the pH to 2 reduced the turbidity (destabilised the emulsion), whereas raising pH to 11 resulted in only minimal changes as compared to the pH neutral case. These observations are consistent with the proposed adsorbed OH⁻ stabilisation mechanism. Addition of electrolyte is expected to screen double-layer repulsions owing to adsorbed OH⁻ and so remove (reduce) any electrostatic barrier to droplet coagulation. Addition of electrolyte (0.1 M NaCl) did affect turbidity, depending upon when introduced in the F-P-T cycles. Only negligible effects were noted if electrolyte was added after de-gassing, or after de-gassing and re-gassing. An interesting observation was that if electrolyte was added prior to degassing then turbidity was much reduced compared to the salt-free system. The paper also claimed that it is not the freeze thaw process that is only responsible for the emulsion stability: it was shown that degassing the oil and water separately and then mixing gave rise to stable emulsions (this introduced controversy into the field, as described below).
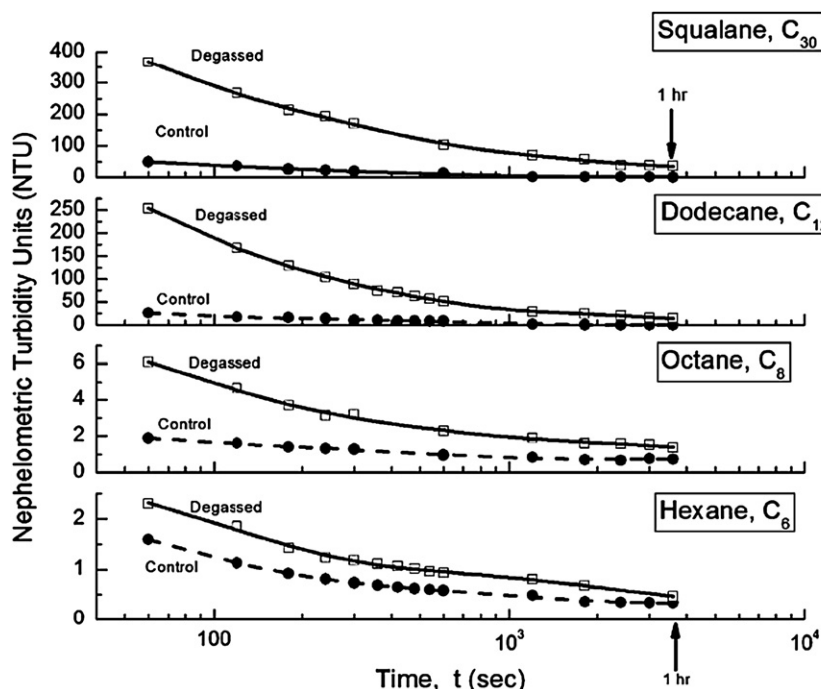
Fig. 3. The NTU measured turbidity of various hydrocarbon in water mixtures both de-gassed (□) and not de-gassed (control, ●) with time, t, after de-gassing and 10 s of shaking by hand. Reprinted from [23] with permission from The American Chemical Society.

These two initial publications [10,23] were subjected to scrutiny by the Bristol group [33]. Firstly, the surface chemical purity of oil was assessed: critically all oils employed in the ANU research were as-received. The classic interfacial tension work of Lunkenheimer [34] had clearly demonstrated that all grades of as-received oils from chemical suppliers contain unacceptable levels of surface-active impurities to be used in any meaningful colloid/interface studies. Treatment and purification protocols for cleaning up commercial hydrocarbon had been proposed, tried and tested [34]: for example, scrubbing with flash chromatography over basic aluminium oxide was shown to restore oil–water interfacial tensions to accepted literature values. To eliminate any possible stabilisation of SFEM's owing to trace surface-active impurities in the alkanes, the Bristol study [33] compared de-gassed aqueous emulsions of commercially available as-received high purity (>99%) and oils surface-chemically purified by alumina chromatography. The reduction of interfacial tension (Fig. 4) owing to the presence of surface active impurities could conceivably provide an additional stabilisation mechanism for SFEM's that had not been considered before [10,23].

The effect of employing "as-received" hydrocarbons as compared to surface chemically pure oils in the freeze-pump-thaw (F-P-T) process showed no noticeable differences, in terms of emulsion formation and turbidity. The conclusions were that any trace surface active impurities present in "as-received" oils are not wholly responsible for SFEM formation. Attention then turned to the F-P-T process itself: de-gassed oil and water mixtures were compared to those that had only undergone freezing and thawing (no pumping to low pressure, therefore no de-gassing). To ensure that this process had not led to partial

degassing, a control sample was subjected to freezing and thawing only, but during thawing air was continually bubbled through the melt. As shown on Fig. 5, all three samples with different treatments produced similar time dependent turbidity decay profiles. These data suggest that de-gassing is not the origin of stabilisation in SFEM's.

An inconsistency between the observations of the Canberrans and Bristolians is whether or not separate de-gassing of oil
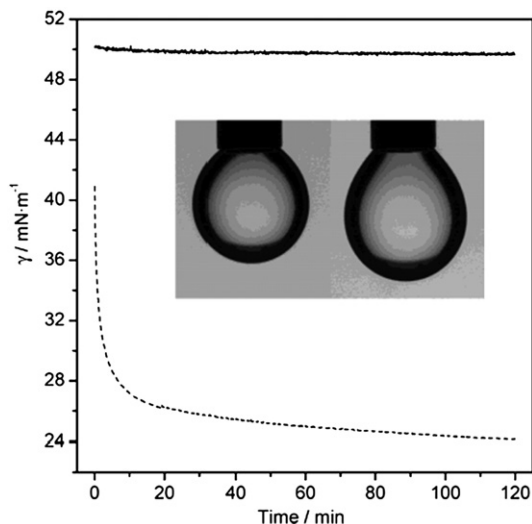

Fig. 4. The time dependence of the oil–water interfacial tension, γ, of n-dodecane determined by the analysis of drop shape. The solid line shows data for purified dodecane, the dashed line for high purity dodecane used 'as received'. The inset shows the initial ($t=0$ min) and final ($t=120$ min) shapes of the unpurified drop. Reprinted from [33] with permission from The American Chemical Society.
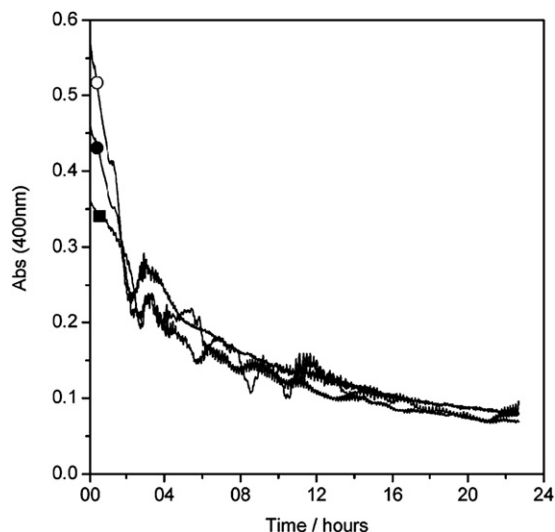
Fig. 5. The time dependence of turbidity of *n*-dodecane in water. As measured by the absorbance of 400 nm light. Series represent samples: de-gassed by freezing, low pressure pumping and thawing cycles, ■; possibly partially de-gassed by freezing and thawing cycles only, ● and not de-gassed by freezing, thawing and having air bubbles passed through, ○. Reprinted from [33] with permission from The American Chemical Society.

and water prior to mixing gives rise to oil droplet dispersions. Maeda et al. [23] suggest that such emulsions are formed, whereas Burnett et al. [33] claim that they are not. Clearly, this is an area where further study is needed.

Burnett et al. suggest a mechanism for the formation of oil droplets in aqueous phases which does not rely on removal of dissolved gas. The mechanism they proposed involves large internal shear forces owing to thermal gradients generated during the extreme temperatures in the freeze thaw process (liquid N_2 to room temperature). Firstly interdiffusion at the oil–water interface may create 'fingers' of oil protruding into the aqueous phase, which are then able to invaginate or bud-off. Secondly, liquid oil may drain into fracture cracks generated in the ice phase during freezing. Oil caught up in these crevasses may be broken away from the bulk oil phase and so become dispersed throughout the water on melting.

5. Cleaning applications

The next paper published in the field attracted attention from journalists in the popular press. In that paper Pashley et al. noted the possible application of de-gassed water as a cleaning agent and ascribed the cavitation theory of hydrophobic interaction reduction to the cause of the effect. Electrical conductivities of these systems as a function of composition, and treatment F-P-T variable were also measured. It was found that de-gassing raises the electrical conductivity of water at 25 °C, from a literature reference value of 0.055 µS cm^{-1} [35,36] to 1.2 µS cm^{-1}.

The proposed cleaning method involves spraying of the dirty item with de-gassed oil, followed in quick succession with a dousing of de-gassed water. De-gassed oil is better dispersed than non-degassed oil so aiding the uptake of the dirt to be removed into the emulsion. This would then be followed by

mechanical agitation and rinsing as per regular washing. The process would be valuable in speciality applications demanding minimal or no surfactant residues, such as for surgical equipment and manufacture/etching of silicon wafers.

The ability of de-gassed water to act as a cleaning agent was tested by following removal of solid hydrophobic 'dirt' (carbon black, graphite and activated charcoal) from standard cellulose filter paper, and also oils (dodecane, squalane, hexamethyldisiloxane and perfluorohexane, none de-gassed) from Pyrex glass surfaces. The removal of the solids from paper was found to be irreproducible; however, better results were observed with oils dodecane and squalane. Turbidities of the emulsions produced in these cleaning applications were similar to those found previously [10,23], such as presented on Fig. 3. Cleaning was also demonstrated using a degassed 0.01 M solution of the cationic detergent cetyl trimethylammonium bromide (CTAB). Surprisingly, the results showed improved cleaning performance after de-gassing. This appears to run contrary to the findings of Zana et al. [28,29] who showed that surfactant properties (cmc) were hardly affected by de-gassing.

Contradictions aside, the ANU group introduced intriguing prospects for detergent-free cleaning applications using de-gassed water. The process is best suited to removal of exceedingly hydrophobic 'dirt', displaying contact angles against water of greater than 90°. For comparison, typical model soils carbon black, graphite and activated charcoal have contact angles against water of <90°, 86° and ∼80°, respectively.

To explore whether or not SFEM's could remain stable for long enough to last the duration of a typical real-life cleaning process, the rate of gas diffusion from the surface of a de-gassed water oil emulsion was also estimated. A model using Fick's second law for one directional gas diffusion though the air–water interface was constructed, with D the diffusion coefficient:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{2}$$

The relevant boundary conditions for this scenario are : at the air–water surface, $x=0$ there is permanently a constant dissolved gas concentration C_0; at time $t=0$ the remaining parts of the system are devoid of any dissolved gas; as time
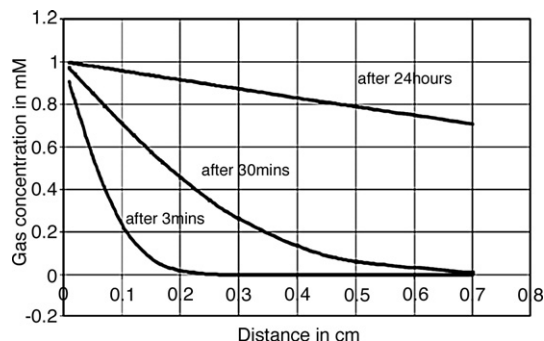

Fig. 6. The calculated diffusion patterns of air into de-gassed water. Reprinted from [8] with permission from The American Chemical Society.

increases the concentration throughout the system tends towards C_0. This leads to a solution of Eq. (2):

$$C = C_0\left[1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right] \qquad (3)$$

Pashley et al. used a series expansion to solve the error function and found that for air diffusing in water ($D=2\times10^{-5}$ cm^2 s^{-1}, at 20 °C, saturation concentration, $C_0=1$ mM) equilibration throughout the system was a slow process, as conveyed by Fig. 6. These represent the slowest possible diffusion times as mechanical action and convection would serve to boost gas solvation. However, Fig. 6 does show that it may be possible to develop practical applications of de-gassed water and oil mixtures as cleaning agents.

6. Pharmaceutical applications

Medical applications were the focus of the next paper to emerge from the ANU group [37]. It is well known that drug molecules are often highly hydrophobic and difficult to administer intravenously without added, potentially toxic surfactants and/or polymers: SFEM's were proposed as alternative delivery vehicles. Similar tests on dispersions to those previously conducted [8,10,20] were carried out on drug carrier oils (perfluorooctyl bromide PFBO, castor and soya bean oils). When employed in conjunction with added surfactants these oils are frequently used as dispersion media for hydrophobic pharmaceuticals, such as the anti-cancer drug Taxol. Reducing the amount of carrier oil required is important as it is possible for the tri-ester linkages to become cleaved through hydrolysis and form unwanted, potentially harmful contaminants.

Turbidity measurements showed that de-gassing aided the dispersion of soya bean oil over castor oil. This seems a little surprising, since soya bean oil has a contact angle against water of 82°, and hence would not be expected to work well in SFEM applications (see section 5). The result was explained by invoking kinetics of chain re-orientation: after creation of fresh oil–water interface soya bean oil would appear to be more hydrophobic, if chain conformations relax slowly and do not immediately exhibit any of their weak hydrophilic character. The suggestion is [37] that for this purpose soy bean oil exhibits a more hydrophobic character than expected. The other oily carrier, PFBO, has a water contact angle of 113°, and so is sufficiently hydrophobic to form de-gassed emulsions in water, as confirmed by turbidity measurements. Emulsion droplet sizes and polydispersities were measured by DLS, suggesting that purifying and de-gassing the oils produced smaller and more monodisperse droplets compared to the natural non-degassed samples. This confers an added benefit to de-gassed emulsions for intravenous drug delivery than similar non-degassed ones.

Phase separation due to creaming of the emulsion occurred after days, as experienced in other studies. However, slow separation may not be a problem for this application, since if gassed oil–water–drug mixtures are stored in airtight containers then SFEM's can be regenerated merely by shaking. The use of de-gassed, aqueous dispersions was qualitatively tested with certain hydrophobic drugs (Propofol, liquid and Griseofulvin, solid) without carrier oils and surfactants; note that both drugs are usually administered with carrier oils and added surfactants. The results were promising with stable dispersions forming for both drugs. The solid drug also formed a stable emulsion when dissolved in de-gassed soya bean oil and dispersed in de-gassed water. The addition of salt was also found not to affect the dispersions. Francis and Pashley's results show that a reduction in the amount of additives in pharmaceutical formulations may be possible SFEM's. Elimination of added surfactants/polymers in drug emulsions could also have significant benefits lowering production costs of and potentially facilitating wider global distribution.

Conceivably SFEM's could be applied to agrochemical formations too. Annual global usage of agrochemical runs to 2.5 million tons [38] ($30 billion p.a. [38]) of pesticides that are normally delivered by emulsion technologies. Another possible application of SFEM's is emulsion polymerisation: industrially important with applications in the manufacture of emulsion paints, adhesives, foamed carpet backings, synthetic rubbers and thermoplastics [39]. Dispersion stabiliser contamination can cause problems during these processes and a reduction in the amount required would benefit the emulsion polymerisation process.

7. Summary

This review has covered the emerging field of surfactant free emulsions (SFEM's), generated by special treatments of water, such as Freeze-Pump-Thaw (F-P-T). Without a shadow of doubt, SFEM's can be readily formed with common components, as long as the systems are subjected to large thermal shocks giving rise to rapid freeze-thaw events. Despite a concerted effort, the mechanisms of formation and stability of these interesting systems still remain controversial, and more effort should be focussed on this. Feasibility of real commercial applications has been demonstrated, notably cleaning and stabilisation of pharmaceutical emulsion formulations: other uses may well emerge in the near future. However, more systematic fundamental research into the physico-chemical origins of the formation and stability is required. Once these points have been explained, and the ideas rigorously tested, creative uses and applications of SFEM's will surely follow.

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