

The dispersion of natural oils in de-gassed water

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Abstract

Recent studies have demonstrated that pure hydrocarbon oils can be dispersed in water as fine droplets without the use of additives. The high interfacial tension between hydrocarbons and water is expected to cause cavitation between oil droplets during separation. This cavitation is aided by dissolved atmospheric gases present in both the oil and water. Their removal allows oil droplets to be readily dispersed in water. In this paper we report on the effect of the de-gassing process on the dispersion of several natural, water immiscible oils. These natural, mixed oils are eucalyptus, lavender and tea tree oil. Although these oils are mixtures and in some cases not as hydrophobic as those used in the earlier studies, the effect of de-gassing substantially enhances their dispersion, producing micron-sized droplets without the need for additives. Dispersions of these natural oils in pure water have a wide range of uses where purity is an advantage, for example, in skin cleaning products and oral sprays.

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1. Introduction

Recent work has demonstrated that fine, micron-sized droplets of oil should be stable when dispersed in water [1]. Oil droplets become charged naturally in water due to the adsorption of hydroxyl ions [2]. These charged droplets remain stable because of the weak van der Waals force between droplets. It has been suggested that the dispersion of fine hydrophobic droplets in water is inhibited by a cavitation process which is expected from an analysis of the thermodynamic processes involved in separating hydrophobic surfaces in water. The interfacial tension between hydrocarbons and water is higher than between hydrocarbons and air or vapour. This is the fundamental reason why separating these surfaces in water will cause cavitation. Further, cavitation creates several forces between the surfaces which will hold the separating droplets together and prevent their dispersion. These include the Laplace pressure and enhanced van der Waals forces, as well as the force opposing the extension of the bridging vapour cavity, as the droplets try to separate. However, the cavitation of water under ambient conditions requires a large input of energy. In practice

it seems that dissolved gases in water act as nucleation sites for this cavitation process and hence removal of these gases inhibits cavitation and so enhances dispersion. It is often forgotten that 20 ml of atmospheric gases are dissolved in a litre of water. These gases can be removed, almost completely, by freezing and thawing under a vacuum [3]. Dispersions can be readily formed, on de-gassing, without the need for stabilising surfactants and polymers. Earlier studies on the effects of de-gassing on dispersion were carried out on pure liquid hydrocarbons and fluorocarbon compounds. The key requirement appears to be that the oil should both water insoluble and hydrophobic, for example, giving a high interfacial tension with water.

The main chemical components present in the natural oils studied in this work are given below:

- Eucalyptus oil: 1,8-cineole ~55%, α -pinene 20–30%, β -pinene ~20–30%.
- Lavender oil: 1,8-cineole 30–35%, linalool 30–40%, camphor 10–25%.
- Tea tree oil: complex mixture of terpinen-4-ol, 1,8-cineole, α -pinene, α -terpinene, γ -terpinene, *cis*-sabinene hydrate.

The organic compounds present in each of these oil mixtures mostly cyclic, non-aromatic, hydrocarbons and linear branched

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chain, partially unsaturated hydrocarbons. In general they either contain no polar groups or one weakly polar group. These oil mixtures are both hydrophobic and water insoluble and so their dispersion in water might be influenced by de-gassing. In this study, we examine the effect of the de-gassing process on the dispersion of these common, natural oils.

2. Materials and methods

Water was prepared by activated charcoal and reverse osmosis filtration prior to distillation and storage in Pyrex vessels in a laminar flow filtered air cabinet. Each of the natural oils were obtained from supermarkets in the ‘purest’ form commercially available and were used without further purification. All preparations and handling of materials for these experiments were carried out in laminar flow cabinets to reduce contamination.

The surface tensions values for each of the natural oils were measured using the rod-in free-surface technique [4]. The RIFS technique typically gives values to an accuracy of about ± 0.1 mN/m. The interfacial tensions between natural oils and water were obtained from analysis of water droplet profiles suspended in each of the oils. This technique gave values to an accuracy of about ± 1 mN/m. The densities of these oils are all less than water. For tea tree oil, eucalyptus and lavender oil the density ranges are: 0.89–0.90, 0.91–0.93 and 0.875–0.888 g/ml, respectively.

Mixtures of various natural oils (typically about 1%) and water, and the separated liquids, were all de-gassed by a process of repeated freezing in liquid nitrogen in a tube sealed by a Teflon tap, followed by pumping down to a pressure of 0.01 mbar (with the tap open) and then melting, with the tap closed, after the tube was pumped down to the target pressure. Any dissolved gas produced on each melting cycle was removed upon re-freezing and pumping. Although this process was carried out five times, typically no further bubbling, on melting, was observed after 3–4 cycles. The vacuum pressure of 0.01 mbar corresponds to a de-gassing level of about 99.999%, if it is assumed that the final pressure achieved after several cycles of freeze/thaw/pumping is given by the pressure in equilibrium with the final frozen liquid, which on being melted does not give any visible bubbling or out-gassing.

Dispersion of oil in water was usually achieved by vigorous shaking of the mixture for 8 sec in a sealed Pyrex tube. Turbidity was measured using an HF Scientific Micro 100 Turbidimeter. Particle sizes and zeta potentials were measured using a Malvern Zetasizer.

The enhancement of oil droplet dispersion in water is most easily monitored using turbidity measurements. This enhancement can be measured by the difference between the new system (de-gassed) and the gassed blank, following vigorous shaking. In each case, the gassed blank was a mixture of the same composition as the de-gassed sample, but was purged with nitrogen gas via a clean pasteur pipette for 10 min. Turbidity is a measure of how many droplets are dispersed in a given phase and is measured in NTU (nephelometric turbidity units). In the results presented here the NTU value was measured via light scattering. To give an understanding of the magnitude of

these turbidity values, distilled water has a turbidity of 0.02 NTU, while tap water has a value of 1–5 NTU. Although useful, NTU measurements are of limited value and the results can be inaccurate if the refractive index of the dispersed phase is close to that of the dispersing phase. For example, visually turbid samples can give low NTU values because their opacity is caused by light absorption rather than scattering. In addition, large droplets, especially for the gassed sample, often stick to the walls of the vessel producing artificially high turbidity values. Hence, in some cases dynamic light scattering (DLS) has been used to obtain the droplet size distribution, as well as the charge on the oil droplets. Careful interpretation of the DLS results is also required for poly-disperse samples. Mono-disperse samples show size distribution by volume graphs (see later) over similar size ranges to the Z-average (diameter) and have a small PDI value (poly-dispersity index). The magnitude of the PDI is a measure of poly-dispersity and for poly-disperse samples the Z-average is accepted as the best estimate of average droplet size. PDI values of 1.0 mean that the sample is very poly-dispersed and contains many large droplets.

3. Results and analysis

3.1. Tea tree oil

The surface tension of purchased tea tree oil was found to be 26.4 mN/m and the interfacial tension with water was 16 mN/m. Dispersions of tea tree oil and water in the range 0.2–0.5 ml in 25 ml water were studied following vigorous shaking after de-gassing or in a nitrogen gassed state (both mixtures at pH 7). The turbidity results shown in Fig. 1 clearly demonstrate the enhanced dispersion created by the de-gassing process. The blank turbidity is often artificially high because of the fact that large droplets of oil often stick to the inner walls of the glass tubes used to store the samples. Particle size measurements shown in Fig. 2 demonstrate the fine droplets dispersed on de-gassing, with an average radius of about 0.8 μm . The dispersion

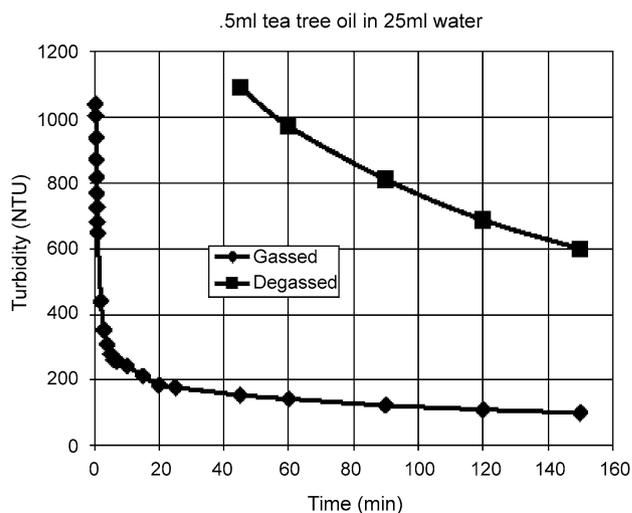


Fig. 1. Turbidity measurements for de-gassed and gassed (blank) tea tree oil in water as a function of time after shaking. Refractive index: 1.4769.

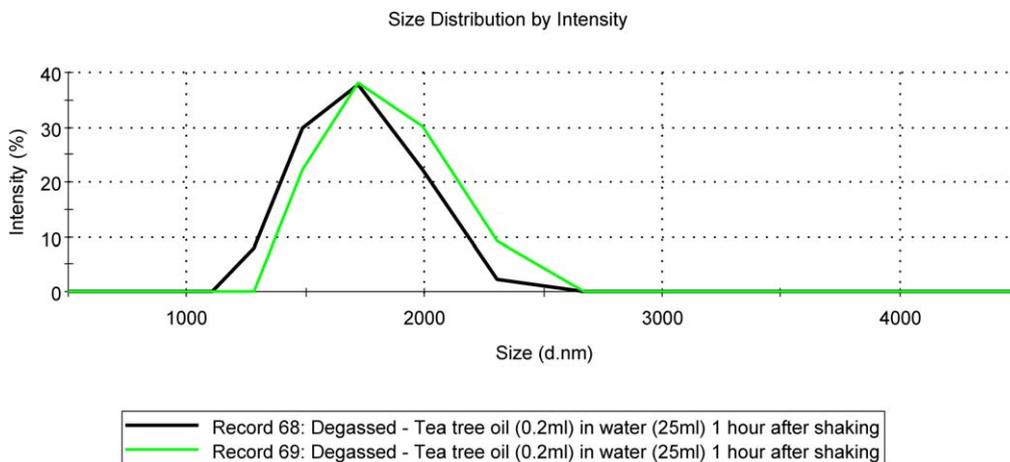


Fig. 2. Particle size data on tea tree oil dispersions, de-gassed dispersions of 0.2 ml of tea tree oil in 25 ml of water. De-gassed: diam. (nm): 1800, Z-average size (nm): 1600, PDI: 0.123. By comparison particle size for gassed (blank) dispersions of 0.2 ml of tea tree oil in 25 ml of water yielded no sensible values. The droplets were large and poly-dispersed. (Z-average size (nm): 1.13×4 , PDI: 1.000.)

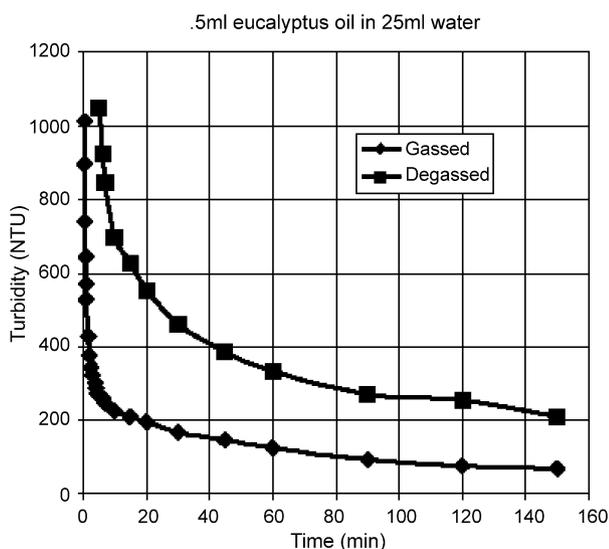


Fig. 3. Turbidity measurements on eucalyptus oil dispersed in water under gassed (blank) and de-gassed conditions. Refractive index of eucalyptus oil: 1.4603.

is fairly mono-dispersed, whereas the gassed (blank) case cannot be measured as it contains many large droplets and is clearly poly-dispersed. Using light scattering the average zeta potential of the de-gassed dispersion droplets of tea tree oil were -35 mV.

3.2. Eucalyptus oil

The surface tension of purchased eucalyptus oil was found to be 25.5 mN/m and the interfacial tension with water was 12 mN/m. Turbidity measurements on eucalyptus oil dispersed in water under gassed (blank) and de-gassed conditions were measured and the results shown in Fig. 3. As for the results with tea tree oil, the de-gassed mixtures gave substantially improved dispersion, shown in Fig. 4. Once again, for the gassed case some large droplets stuck to the inside of the glass tube in which the mixtures were shaken, so the particle size distribution was also measured. The de-gassed dispersion gave particles in the range of $1\text{--}2$ μm radius. By comparison, the gassed samples gave poly-disperse samples for which sensible values could not be obtained. The zeta potential of the de-gassed dispersion

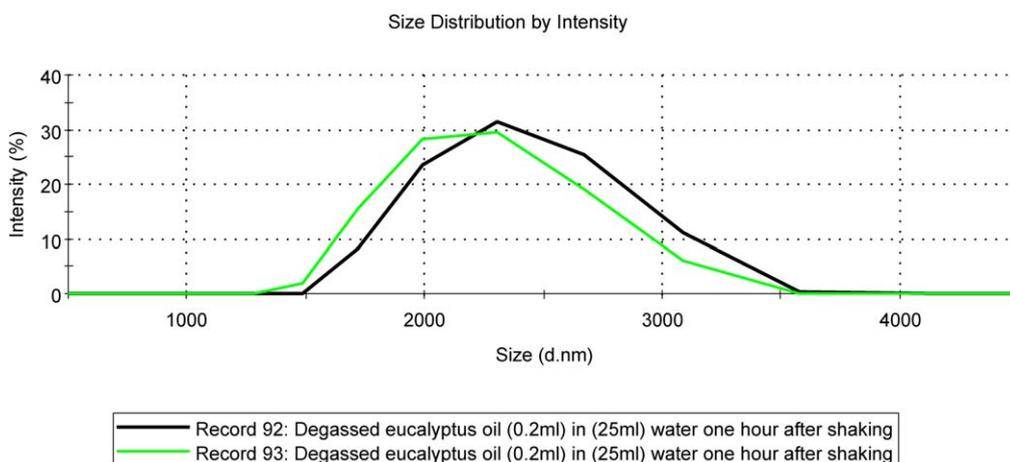


Fig. 4. Particle size measurements on eucalyptus oil dispersed in water under de-gassed conditions. De-gassed: diam. (nm): 2220, Z-average size (nm): 3590, PDI: 0.330.

droplets was found to be -47 mV, which is close to the value reported for pure hydrocarbons.

3.3. Lavender oil

The surface tension of purchased lavender oil was found to be 25.6 mN/m and the interfacial tension with water was 13 mN/m. The effect of de-gassing on the turbidity of shaken mixtures of lavender oil and water is shown in Fig. 5. Clearly, once again de-gassing substantially increases the dispersion of this natural oil in water. Light scattering measurements of the resulting particle size distribution are shown in Fig. 6. The oil droplets are fairly mono-dispersed with an average particles radius of about 1.5 μm . The average zeta potential of these particles was found to be -41 mV, comparable with results obtained on hydrocarbon liquids. By comparison, as for the other oils studied, the gassed case gave highly poly-dispersed samples for which sensible data could not be obtained. A photograph of the effects of de-gassing on these dispersions is shown in Fig. 7.

The significant effect of de-gassing on the dispersion of each of these natural oils in water is remarkable and especially interesting because of their interfacial tensions with both air and

water. Cavitation is expected for pure hydrocarbon oil droplets, such as dodecane, separated in water [1], because of the low surface tension of dodecane (25.4 mN/m) and its high interfacial tension (52.9 mN/m) with water. That is, cavitation creates the lower energy, oil/air interfaces, rather than the higher energy, oil/water interfaces. However, we would not expect de-gassing to enhance the dispersion of these natural oils because, in each case, their surface tensions are higher than the corresponding interfacial tension with water.

Another way of considering this is through the concept of a theoretical water droplet contact angle formed on the surface of the oil in air. Hence, using the Young equation (see Fig. 8)

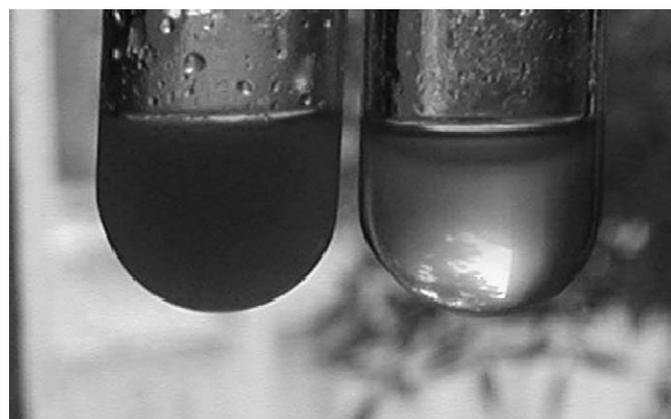


Fig. 7. Lavender oil and water. The de-gassed mixture is on the left. Photo taken minutes after shaking.

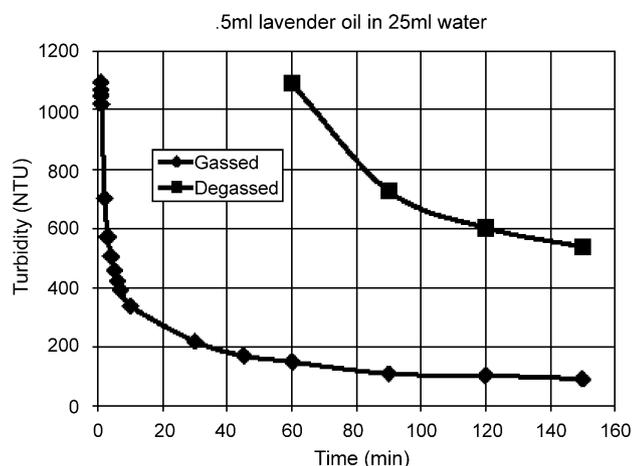


Fig. 5. Turbidity of lavender oil under de-gassed and gassed conditions. Refractive index: 1.4690.

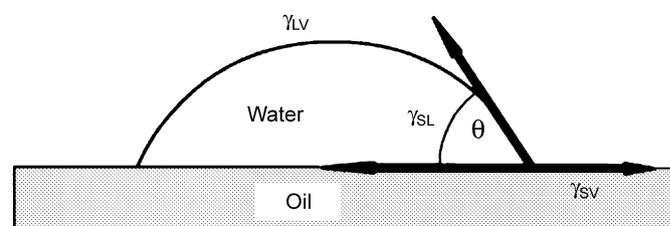


Fig. 8. Droplet profile showing the Young equation. Young's wetting equation is derived from a balance of the forces at the three-phase line: $\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$.

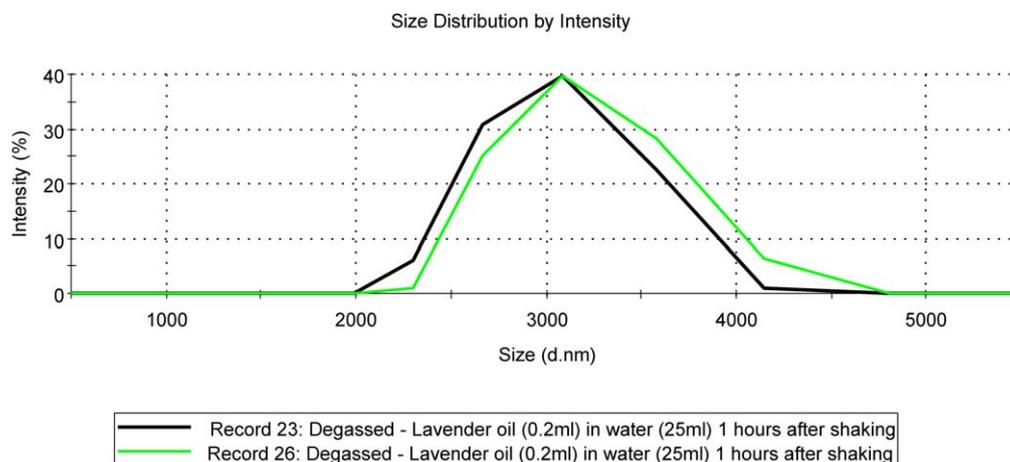


Fig. 6. Particle size measurements on de-gassed samples of lavender oil and water. De-gassed: diam. (nm): 3180, Z-average size (nm): 2880, PDI: 0.194.

for water droplets on dodecane, the theoretical contact angle is 112° . This high angle, $>90^\circ$, indicates that air ‘wets’ the oil surface better than water. The oil is very hydrophobic. If we apply the same analysis to the three oils, tea tree oil, eucalyptus and lavender oil, we calculate theoretical water contact angles of 82° , 79° and 80° , respectively. Hence, although all of these oils are hydrophobic, they are not more hydrophobic than air and so we might expect de-gassing to have no effect. This is because the air/natural oil interface has a higher energy than the water/natural oil interface.

In earlier work, soybean oil [5] was also found to be more readily dispersed in de-gassed water, even though the interfacial tension with water was low. These observations were explained by the high molecular weight of soybean oil and the slight amphiphilic nature of the triple ester group. Thus, when measuring surface and interfacial tensions, large molecules can orientate to produce a lower tension. However, during vigorous shaking, the rapid dispersion process does not allow the high molecular weight molecules to orientate at the rapidly formed new surfaces of the droplets and so the system behaves much more like a pure liquid hydrocarbon.

This effect may occur for some of the high molecular weight components of these natural oils, for example camphor. However, a second effect will be caused by the presence of slightly polar component molecules, such as cineole, in a mostly non-polar liquid of, say, α -pinene and terpinene. Polar components will diffuse to the surface or interface to lower the tension during static, equilibrium measurements. However, during rapid and vigorous shaking, this diffusion to the new surfaces formed will not be possible. Hence, again these multi-component oils will behave closer to pure hydrocarbons under these conditions, as observed here. These results taken together with those re-

ported earlier indicate that interfacial tension values are useful in predicting the effects of cavitation on dispersion, but only for pure, non-polar liquids.

4. Conclusions

A range of natural oils, insoluble in water, can be dispersed in pure water as micron-sized droplets by the use of a freeze–thaw de-gassing process followed by vigorous shaking. These dispersions could be used for a wide range of purposes, such as for natural perfumes, skin cleaning mixtures, etc. If they are stored in sealed vessels the dispersion can be regenerated simply by shaking, after gravity settling. They offer a pure source of these natural oils for many applications where there is a need to remove other additives, often used to stabilise these dispersions as emulsions. Continuous agitation or freezing, after formation, will prevent gravity settling of the dispersions, so that the particle size distribution can be precisely controlled and maintained, if required. The de-gassing process will also reduce the rate at which these natural oils degrade, because of the absence of dissolved oxygen, when stored in sealed vessels.

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