The removal of thermally-aged films of triacylglygerides by surfactant solutions.

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Abstract

Thermal ageing of triacylglycerides (TAGs) at high temperatures produces films which resist removal using aqueous surfactant solutions. We have used a mass loss method to investigate the removal of thermally-aged TAG films from hard surfaces using aqueous solutions of surfactants of different charge types. It is found that cationic surfactants are most effective at high pH, whereas anionics are most effective at low pH and non-ionic surfactant is most effective at intermediate pH. We show that the TAG film removal process occurs in several stages. In the first “lag phase” no TAG removal occurs; the surfactant first partitions into the thermally-aged film. In the second stage, the TAG film containing surfactant is removed by solubilisation into micelles in the aqueous solution. The effects of pH and surfactant charge on the TAG removal process correlate with the effects of these variables on the extent of surfactant partitioning to the TAG film and on the maximum extent of TAG solubilisation within the micelles. Additionally, we show how the TAG removal is enhanced by the addition of amphiphilic additives such as alcohols which act as co-surfactants. The study demonstrates that aqueous surfactant solutions provide a viable and more benign alternative to current methods for the removal of thermally-aged TAG films.

Keywords

Thermally-aged triacylglycerides, TAG, surfactants, solubilisation, micelles

1. Introduction

The removal of stains consisting of liquid triacylgleride (TAG) mixtures from fabric and hard surfaces by surfactant solutions has been much studied in order to optimise the efficacy of commercial detergents[1-8]. The key mechanisms involve either “roll-up” of the TAG drops to form emulsion drops within the solution or solubilisation of the TAGs within the micelles of the surfactant solution. Optimal TAG removal generally occurs under conditions when the aqueous surfactant solution system exhibits minimum interfacial tension with the liquid TAG phase and the surfactant shows maximum solubilisation of the TAG. This condition corresponds to microemulsion phase inversion of the system at equilibrium which, in turn, is also the condition required for emulsion phase inversion of the system containing equal volumes of the oily TAG phase and aqueous solution. Much less attention has been given to the removal of thermally-aged TAG mixtures by surfactant solutions where baking causes the TAG mixture to be hardened to a solid or semi-solid. Industrial cleaning of thermally-aged, hardened TAG residues on cooking surfaces is commonly done using alkaline solutions which act by chemically hydrolysing the TAG species to glycerol and fatty acid salts which are then easily removed by water rinsing. The focus of this work is to investigate how thermally-aged, hardened TAG films on glass surfaces can be removed using surfactant solutions.

Baking of TAG films at the temperatures used in food preparation causes complex chemical and physical changes in the TAG mixture[9-18]. The main chemical reactions are hydrolysis of the TAGs to produce fatty acids and di- or mono-glycerides and glycerol, oxidation which reduces the concentration of unsaturated fatty acid species and increases the total polar content and polymerisation reactions to give a variety of cyclic dimers and acyclic polymers. These chemical changes are accompanied by physical changes including increases in colour, viscosity and foamability plus (as for the TAG system investigated here) conversion of a liquid oil to a semi-solid. The chemical and physical changes in fats during baking are the result of a complex and incompletely understood series of reactions which depend strongly on the nature of the TAG species, temperature, oxygen content, trace level catalytic species, the nature of the surface of the container and its surface:volume ratio.

In this study, we focus on a standard TAG mixture which is commonly used to assess the effectiveness of different cleaning formulations. This mixture consists of 33.3 wt% lard (pig fat), 33.3 wt% vegetable oil (rapeseed oil, supplied as Tesco’s own brand) and 33.3 wt% vegetable shortening (which, in turn, consists of 50 wt% cottonseed oil and 50 wt% soya bean oil, Crisco brand). Before thermal ageing, this triglyceride mixture is a semi-solid at room temperature and is a pale yellow liquid at 40^{o}C which is the temperature used here to determine the extent of removal. The unbaked, liquid TAG film is easily and quickly cleaned using aqueous surfactant solutions. When thermally aged using the procedure detailed below, the TAG mixture at 40^{o}C is a light-brown, rubbery and tacky semi-solid which is much more difficult to clean from a surface using aqueous surfactant. The aims of this study are to investigate the conditions required to remove thermally aged TAG films from hard surfaces using aqueous surfactant solutions and to elucidate the mechanism of the process. We address the following issues.

- How do the conditions used for the thermal ageing of the TAG film affect its chemical and physical properties and its removal by surfactant solutions?
- How does the thermally aged TAG film removal depend on the surfactant concentration, pH, the nature of the surfactant and temperature?
- How do the surfactants interact with the thermally aged TAG film during the removal?
- Can the TAG film removal be enhanced by additives to the surfactant solutions?

2. Experimental

2.1 Materials.

Water was purified by passing through an Elgastat Prima reverse osmosis unit followed by a Millipore Milli-Q reagent water system. Its surface tension was 71.9 mN m^{-1} at 25°C, in good agreement with literature. The standard TAG mixture used consists of 33.3 wt% lard (pig fat, supplied as Sainsbury'a own brand), 33.3 wt% vegetable oil (rapeseed oil, supplied as Tesco's own brand) and 33.3 wt% vegetable shortening (taken to consist of 50 wt% cottonseed oil and 50 wt% soya bean oil, Crisco brand), mixed together as liquid at 40^{o}C for 30 minutes. Thermally aged TAG films were prepared by pipetting the molten TAG mixture onto a masked glass slide (the back surface of the slide and the two ends were masked with sacrificial glass pieces held by spring clips). This creates a TAG film of a fairly constant mass (0.2 - 0.25 g) and constant surface area (14.3 cm^2) on one side of the slide. To make thermally aged TAG films, the slides were laid flat on a tray and placed in an oven for 1 hour at 200^{o}C (except where noted otherwise). According to ref. 19, the composition of the TAG mixture expressed as the wt% of the fatty acids present in the mixture of oils is as shown in Table 1.

The cationic surfactant with tradename BTC65 was supplied by Stepan as a 50 wt% solution in water. The active material contains a mixture of alkylbenzyldimethylammonium chloride species with a distribution of hydrophobic chain lengths from C8-C18. Titration of the dried solid material showed the average structure was tridecylbenzyldimethylammonium chloride (abbreviated here as TBDMAC). The anionic surfactant with tradename Bioterge PAS 8S from Surfachem was supplied as a 20.4 wt% solution in water and consists of sodium octyl sulphate (SOS). Sodium dodecyl sulphate (SDS) was supplied by Sigma-Aldrich and was 95% pure. The non-ionic surfactant with tradename Neodol 91-6 from Surfachem is 100% alkyl ethoxylate with a distribution on both the alkyl and ethoxylate chain lengths. The average structure is $H\text{-}(CH_2)_{10}\text{-}(O\text{-}CH_2\text{-}CH_2)_6\text{-}OH$ and is denoted C10E6 here.

The acids, bases and buffers, monosodium phosphate (Sigma, >99%), disodium phosphate (Sigma, >98%), citric acid (Aldrich, >99.5%), sodium citrate (Aldrich, >99%), sodium tetraborate decahydrate (Sigma, >99.5%), HCl (Fisher, Analytical grade) and NaOH (Fisher, 99%), were used as supplied. Reagents for the Epton and iodine number titrations, Wijs solution (Fluka), KI (Fisher, >99.5%), sodium thiosulphate (Fisher, >99.95%), chloroform (Fisher, >99%), Patent blue VF (Sigma, 50%), dimidium bromide (Sigma, 95%), and sulphuric acid (Fisher reagent grade), were used as supplied. The additives, 1-dodecene (Aldrich, 99%), 1-decanol (Aldrich, 99%), 1-butanol (Riedal-de-Haen, >99%), 1-propanol (Fisher, >99%), methanol (Fisher, >99%), n-decane (Aldrich, >99%), 1-heptanol (Aldrich, 98%), 1-pentanol (Lancaster, >98%), 1-hexadecanol (Aldrich, 99%) and anisole (Sigma, 99%), were used as supplied.

2.2 Methods.

The iodine value of the TAG mixture (equal to the mass of iodine in grams that is consumed by 100 grams of the substance) is a measure of the amount of unsaturated species in the sample and was determined as follows. A known mass of the TAG mixture is mixed with chloroform and an excess of Wij's solution, consisting of a standardised mixture of iodine monochloride in acetic acid, and left in the dark with vigorous stirring for one hour. An excess of potassium iodide is added which reacts with the unreacted ClI to liberate iodine which is then titrated against sodium thiosulphate. The overall reaction sequence is:

$$\text{R-CH=CH-R' + excess ClI} \rightarrow \text{R-CHI-CHCl-R' + remaining ClI}$$
$$\text{Remaining ClI + excess KI} \rightarrow \text{KCl} + I_2$$

$$2\,Na_2S_2O_3 + I_2 \quad \rightarrow \quad Na_2S_4O_6 + 2\,NaI$$

All aqueous surfactant solutions were prepared to have pH values of either 1, 4, 7 or 10. In addition to the added surfactant, the electrolyte contents of these solutions were pH 1: 100 mM HCl; pH 4: 62 mM citric acid + 38 mM sodium citrate; pH 7: 58 mM monosodium phosphate + 42 mM disodium phosphate and pH 10: 59 mM NaOH + 41 mM sodium tetraborate. To measure TAG film removal as a function of time, a pre-weighed slide coated with a TAG film is held vertically in a beaker and completely immersed in 250 mL of the cleaning solution which is vigorously stirred and thermostatted. At regular intervals the slide is removed, gently rinsed under a stream of deionised water, dried in a desiccator under reduced pressure and reweighed. The percentage change of the original mass of the TAG film is used as a measure of TAG loss by cleaning.

Analysis of the ionic surfactant concentrations in both the aqueous solution and TAG phases was made using the two-phase titration method detailed in ref. 20. Surfactant samples in thermally aged TAG phases were dissolved in the chloroform phase of the two-phase titration system. It was checked using TAG samples containing added known concentrations of anionic or cationic surfactant that the presence of the TAG mixture did not affect the titration. Additional “blank” titrations of either untreated or thermally aged TAG mixture samples containing no added ionic surfactant showed no detectable anionic or cationic surface active species (e.g. free fatty acid salts). If present, the concentrations of such species was estimated to be less than 0.04 mM. Analysis of the non-ionic surfactant was done using the method of Tsubouchi andTanaka[21] which involves complexation of the non-ionic with tetraphenylborate in a two-phase titration. For titration with thermally aged TAG samples, it was found necessary to increase the concentration of the Victoria Blue B indicator to improve the visibility of the end-point because of the colour of the TAG films. Titre results for samples of non-ionic surfactant in TAG films did require significant correction (approx. 10% or less) for the presence of the TAG species, i.e. titre values of “blank” titrations of TAG samples containing no surfactant were subtracted.

Scanning electron microscope (SEM) images were obtained using a Hitachi TM1000 instrument operating in high vacuum mode. Samples were coated in a thin film of gold prior to imaging.

Differential scanning calorimeter (DSC) measurements of thermally aged and untreated TAG samples were made using a Mettler Toledo DSC822 instrument. Samples were weighed into aluminium pans and sealed with lids with an identical empty pan as reference. Using a heating/cooling rate of 5^{o}C/minute, samples were initially heated to 90^{o}C, held at 90^{o}C for 5 minutes, cooled to -20^{o}C, held at -20^{o}C for 5 minutes, heated to 90^{o}C, held at 90^{o}C for 5 minutes and finally cooled back to -20^{o}C. In this way, two consecutive heating and cooling cycles were recorded for each sample.

3. Results and Discussion

3.1 How do thermal ageing conditions affect the properties and removal of baked TAG films?

The iodine values of the TAG film samples before and after different thermal treatments were measured, as shown in Table 2. A theoretical iodine value for the unbaked TAG mixture based on the composition given in Table 1 is 46.3, in reasonably good agreement with the value measured here (47.1 ± 0.4, Table 2). Baking of the TAG films at 150^{o}C for up to 3 hours has no significant effect on the iodine value. However, baking at 200^{o}C for 1 hour reduces the iodine value to approximately 21, indicating an approximately two-fold reduction in the amount of unsaturated species. Baking for longer or at a higher temperature has no further effect on the iodine value.

The concentration of free fatty acid salts produced by triglyceride hydrolysis of the TAG mixture was determined by Epton titration using a cationic surfactant as titrant. For either baked or untreated TAG films, the concentration of anionic fatty acid salts was found to be less than 0.04 mM from two-phase titration results. However, it should be noted here that the pH of the aqueous phase in these titrations was 4.5. At this pH, virtually all of the total free fatty acid present would be in the form of uncharged, protonated fatty acid which is likely to partition from the water to the oily, TAG phase where its presence would not be revealed by this titration.

DSC heating and cooling curves for thermally aged and untreated TAG samples are shown in Figure 1. When heated at 5^{o}C/minute, the untreated TAG mixture shows endothermic (melting) peaks at approximately -13, 30 and 47^{o}C and melting appears to be complete by 50^{o}C. The unbaked TAG mixture is observed to be semi-solid at room temperature, presumably due to the formation of a fat crystal network. When thermostatted at 40^{o}C, the unbaked TAG mixture is a yellowish liquid with no visible fat crystals. Following thermal ageing of the TAG mixture for 1 hour at 200^{o}C, the relatively narrow heat flow peaks are greatly broadened and shifted to lower temperatures. These results indicate that the changes occurring during thermal treatment cause the TAG mixture to lose its melting/crystallisation peaks at clearly defined temperatures. In appearance, the thermally aged TAG films remain semi-solid when thermostatted at 40^{o}C and have a rubbery, tacky feel.

Overall, thermal-ageing of the TAG for 1 hour at 200^{o}C causes (i) a two-fold reduction in double bond content; (ii) a broadening of the melting/crystallisation temperature range and (iii) a change in state from liquid to a rubbery, tacky semi-solid at 40^{o}C. The free fatty acid content following baking has not been determined. Thermal treatment at higher temperatures or longer times do not induce further changes in the appearance or level of unsaturation. With respect to TAG film removal by surfactant solutions at 40^{o}C, a film of the unbaked liquid TAG mixture was completely removed in approximately 1 minute by 43 mM TBDMAC (cationic) surfactant solution at pH 10. The thermally aged TAG films are much more difficult to remove as shown in Figure 2. For 43 mM TBDMAC (cationic) surfactant solution at pH 10 and 40^{o}C, complete film removal requires several hundred minutes. Consistent with the observations that the key thermally-induced changes in the TAG mixture are complete after 1 hour at 200^{o}C, it can be seen from Figure 2 that the rates and extents of removal by the cationic surfactant solution of TAG films baked at either 200^{o}C for 1 hour or 250^{o}C for 3 hours are not significantly different. Because of this, all further measurements of baked TAG films used films which were thermally-aged at 200^{o}C for 1 hour.

3.2 How is thermally-aged TAG film removal affected by the conditions used?

Figure 3 shows percentage TAG film removal by a surfactant solution versus time (on a logarithmic scale) for baked TAG films of different thicknesses but constant surface area. The shapes of the film removal plots reveal some important mechanistic features. Firstly, the plots all show a lag time of about 30 minutes over which no TAG removal occurs. Importantly, this lag time is independent of the TAG film thickness. As seen later, this lag time is related to the time required for the surfactant to penetrate and partition to the fat film from the aqueous solution. If the lag time corresponded to the time required for the surfactant to diffuse across the complete depth of the TAG film (and thereby affect the adhesion of the fat film with the underlying glass substrate), the lag time should be proportional to the square of the fat film thickness. Figure 3 shows this is *not* the case; it appears that the lag time corresponds to the time required for the surfactant to penetrate only into the outermost surface of the TAG film.

Following the lag time, the TAG film is removed by the surfactant solution which is observed to remain transparent and weakly scattering. This weak scattering indicates that the TAG removed into solution is present in objects of size much less than the wavelength of light, i.e. it is solubilised into nm-sized micelles rather than micrometre-sized emulsion drops. The post-lag-phase rate of TAG removal by solubilisation decreases slightly as the amount of TAG mixture in the film is increased. Under the conditions used here (250 ml of 43 mM cationic surfactant), the TAG films containing 0.16 and 0.25 g of TAG mixture are completely removed and solubilised into the surfactant solution whereas for the film with 0.46 g TAG mixture, only 0.36 g is removed. This incomplete removal is presumably due to the limit of maximum solubilisation of the TAG by the surfactant micelles being reached in this case. This maximum solubilisation capacity corresponds to 0.36/(0.25 x 0.043) = 33 g of fat per mol of surfactant. The decrease in rate of removal by solubilisation observed for systems with increasing initial mass of TAG is probably due to the decrease in available solubilisation capacity of the aqueous surfactant solution.

The effect of increasing the surfactant concentration on the TAG film removal rate is shown in Figure 4. The lag time is unaffected by the surfactant concentration but the post-lag-phase rate of removal by solubilisation increases with increased surfactant concentration, presumably because the increased surfactant concentration leads to an increased fat solubilisation capacity of the aqueous surfactant solution.

We have investigated how the rate and extent of baked TAG film removal is dependent on the charge type of the surfactant and the pH of the surfactant solution as shown in Figure 5. Control measurements with solutions of the same pH but no surfactant all showed zero baked TAG film removal. Several observations are noteworthy here. Firstly, the ionic surfactants (anionic or cationic) all cause either no change in the mass of fat remaining or its progressive removal. In contrast, the non-ionic surfactant generally causes an initial mass *gain* of the TAG film during the lag phase. This shown on the graph as a *negative* mass loss. This observation suggests there may be differences in the mechanism of TAG film removal by non-ionic versus ionic surfactants. The observed mass gain with non-ionic surfactant in the lag phase may be associated with entry of a significant mass of water into the baked TAG film associated with non-ionic surfactant partitioning.

Secondly, we find the previously unsuspected result that, at high pH, the cationic surfactant is the most effective whereas the anionic is most effective at low pH and the non-ionic is most effective at intermediate pH. This pH effect on TAG film removal correlates with pH effects on the maximum extent of TAG solubilisation in the solutions of the different surfactants, as seen in Figure 6. Note that the values of maximum TAG film mass lost in Figure 6 are derived from the long-time plateau values from Figure 5 in the cases where this corresponds to less than 100% of the total TAG present. In the other cases, the maximum mass of TAG solubilised (lost) was measured in additional experiments using larger amounts of added thermally aged TAG mixture. These results suggest that the cationic surfactant micelles are best at solubilising TAG when the solutions contain high concentrations of anionic hydroxide ion counterions (i.e. high pH) attracted to the micelles whereas anionic surfactant micelles solubilise best in the presence of high concentrations of cationic hydrogen ions (i.e. low pH). The non-ionic surfactant solubilises best at neutral pH when the concentrations of both hydrogen and hydroxide ions are very low.

In general, aqueous surfactant solutions at concentrations above their critical micelle concentration (cmc) contain a mixture of surfactant monomers and micelles in rapid dynamic equilibrium. The aqueous monomer concentration is approximately equal to the cmc and the concentration of micellised surfactant is equal to the total surfactant concentration minus the cmc. Because only the micellised surfactant is capable of fat solubilisation, the maximum extent of fat solubilisation and its variation with pH depends on both the cmc and the properties of the particular micelles. Values of the cmc for the different systems are summarised in Table 3. For the anionic surfactant SOS, the cmc is similar in magnitude to the overall surfactant concentration of 43 mM used for the cleaning measurements and hence the cmc value is a significant factor in determining the overall fat solubilisation capacity for the SOS solutions used here. The cmc values for SDS, TBDMAC and C10E6 are all small relative to the total surfactant concentrations used here. In these cases, the great majority of the total surfactant present is in the form of micelles capable of fat solubilisation and hence the pH dependence of the cmc is not a significant factor in the pH dependence of the solubilisation capacity. The maximum extents of TAG solubilisation for the anionic surfactants SOS (high cmc) and SDS (low cmc) are compared in Figure 6. Because of its lower cmc, SDS shows much greater solubilisation than SOS at all pH values except at the lowest pH of 1 where the cmc of SOS is reduced to about half the total surfactant concentration. At pH 1, the solubilisation values of SOS and SDS are similar.

Figure 7 shows the effect of temperature on the thermally aged TAG film removal rate for the cationic surfactant at pH 10. Lowering the temperature from 40^{o}C to 10^{o}C causes the lag time to be dramatically increased from about 30 minutes to about 1000 minutes and also slows the rate of TAG removal in the post-lag phase. Possible factors contributing to this temperature effect may include alteration in the thermally-aged TAG film structure (e.g. increased solidification) causing a decrease in the rate and/or extent of surfactant partitioning from the water to the film and changes in the extent of TAG solubilisation in the surfactant micelles. Further measurements, beyond the scope of this work, would be required to resolve which of these factors are dominant.

Figure 8 shows illustrative SEM images of the thermally aged TAG films before and at various stages during removal with different surfactant solutions. Before immersion in surfactant cleaning solution (top image), the thermally aged TAG film surface is fairly smooth but shows a network of fine lines. The lines may correspond to either crystallite boundaries or indicate some degree of microphase separation within the TAG films. After immersion in cationic TDBMAC cleaning solution at pH 10 for 50 minutes (middle image, corresponding to the lag phase being complete and approximately 10% of the TAG removed, see Figure 5), the surface is still fairly smooth but the network of fine lines is more pronounced; this suggests that these points in the film are removed by the surfactant first. After immersion in non-ionic C10E6 solution at pH 7 for 80 minutes (bottom image), the film is less smooth and the network of fine lines appears to be converted to a pattern of surface bumps. From Figure 5, it can be seen that this latter image corresponds to part-way through the cleaning lag phase in which immersion in the non-ionic surfactant solution causes a slight mass *gain* of the fat film. The mass gain and change in appearance of the fat film maybe due to ingress of surfactant plus some water into the film. Overall, these SEM images (plus many others not shown here) reveal that the thermally aged TAG films are slowly eroded by the surfactant cleaning solutions with only minor changes in surface appearance. Under the conditions used here, surfactant solution cleaning does not lead to flaking or removal of macroscopic large fragments of the TAG films.

3.3 How do the surfactants interact with the thermally-aged TAG films during removal?

Thermally-aged TAG films were immersed in surfactant solutions, removed at different times and analysed for surfactant content in the TAG films. Figure 9 shows examples of the measured surfactant concentrations in the TAG films as a function of immersion time. For the cationic surfactant TBDMAC, partitioning to the thermally aged TAG is high at pH 10 but much lower at pH 1. This pH dependence is reversed for the anionic surfactant SOS; partitioning is high at pH and low for pH 10. Similarly to the variation of the maximum extent of TAG solubilisation, the dependences of the partitioning on pH and surfactant headgroup charge correlate with the effects of these variables on the overall cleaning process as seen in Figure 5. It can also be seen that the timescales over which surfactant partitioning to the TAG films occurs are similar to the lag times observed in the TAG removal plots of Figure 5.

For the experiments described here, potential complications could arise from chemical degradation of the surfactants, particularly at the low and high pH values used. For example, it is well known that alkyl sulphate hydrolysis is accelerated at both low and high pH. Using measurements of the extent of surfactant degradation (not shown here) over time when incubated at different pH and temperatures, it was concluded that surfactant loss by chemical degradation at 40°C over the 5 hour duration of a typical TAG film removal/partitioning experiment was negligibly small for all the pH values used.

The extents of surfactant partitioning were expressed as values of the TAG-water partition coefficient K_{ow} defined as $[\text{surfactant}]_{TAG}/[\text{surfactant}]_{water}$ and were measured for both thermally aged and untreated (liquid) TAG at 40°C. For the K_{ow} measurements, the relative volumes of the TAG and aqueous phases and the surfactant concentrations were altered to overcome problems arising from TAG solubilisation within the surfactant solutions. Two main points emerge from the plots shown in Figure 10. Firstly, the variation of K_{ow} with pH for the thermally aged TAG systems correlates well with the TAG film removal behaviour shown in Figure 5, i.e. partitioning and cleaning are high for cationic surfactant at high pH, high for anionic surfactants at low pH and high for non-ionic at intermediate pH. Secondly, comparison of the K_{ow} values for baked and unbaked fat shows that the K_{ow} values for untreated TAG mixtures are 1-2 orders of magnitude less than for the thermally aged TAG mixtures. Clearly, the thermal ageing process produces TAG oxidation and/or other species that increase the affinity of the TAG mixtures for the different surfactants. Although the exact identities of the species produced by thermal treatment are currently unclear, they are likely to include free fatty acids, mono- and di-glycerides and glycerol (from hydrolysis), polar species from oxidation and polymeric species. Understanding precisely how such species increase the affinity for the different surfactants in the pH dependent ways seen here would require additional study which is beyond the scope of this paper.

In general, the partitioning of ionic species from aqueous solution to a low polarity solvent like the TAG mixture is energetically unfavourable. Depending on the dielectric constant of the low polarity solvent, ionic species are unlikely to be present in the low polarity solvent as dissociated ions; they are expected to be present as uncharged ion pairs. For the anionic surfactant ions considered here (alkyl sulphates), the relatively high partitioning at low pH could, in principle, be a result of protonation of the alkyl sulphate ion to form an uncharged species able to partition to the TAG phase. However, the pKa of the conjugate acid of a methyl sulphate ion is estimated to be approximately -3.4[24]. Assuming the conjugate acids of octyl and dodecyl sulphate ions are similarly strong, it can be seen that significant protonation of the anionic surfactant ions is not expected to occur, even at the lowest pH of 1 used here. Hence, it appears likely that the anionic surfactant species partition into the baked fat as uncharged species formed by ion-pairing with a cationic counter-ion other than H^+ which is present in the buffer electrolytes used here (see experimental section 2.2). Similarly, the cationic surfactant ions are likely to partition to the fat in the form of uncharged ion-pairs with either OH^- or alternative anions from the buffer electrolytes present. Hence, it might be anticipated that the tendency of the ionic surfactants to partition to the TAG phase may depend on the nature and concentration of the counter-ions present.

From the results presented above, the mechanism of the removal of thermally aged TAG films by these surfactant solutions first involves partitioning of the surfactant from the solution into the TAG over a period of several 10s of minutes. No TAG removal occurs during this process which corresponds to the lag time of the removal process. Once a certain surfactant concentration in the TAG film is achieved at a time equal to the lag time, removal of the TAG from the film into the solution occurs. In its final state, the removed TAG is solubilised within aqueous micelles. It appears that the TAG solubilisation into the micelles occurs via self assembly of the surfactant + TAG within the TAG film followed by exit of the TAG-filled micelles into the water, i.e. the surfactant must partition to the TAG film before this solubilisation can occur. If this hypothesised mechanism is correct, then it is predicted that adding surfactant to the TAG film prior to immersion and cleaning in a surfactant solution should remove the lag time and cause TAG removal to commence promptly on immersion in the solution. Figure 11 shows that this predicted behaviour is indeed observed. For the cationic surfactant TBDMAC at pH 10, the plot of percentage TAG removed versus immersion time for a TAG film without added surfactant shows a lag time of approximately 30 minutes. When the TAG film is “doped” with 10 mM TBDMAC prior to immersion in 43 mM TBDMAC solution, the TAG film removal commences immediately with no lag time. A doped TAG film immersed in water at pH 10 containing no surfactant shows no removal. This control experiment suggests that the TAG film doping level of 10 mM TBDMAC used requires dynamic replenishment from the aqueous solution before TAG removal by solubilisation into aqueous micelles can occur.

3.4 Can the thermally-aged TAG film removal be enhanced by additives?

From the range of systems investigated here, the best removal of thermally-aged TAG films occurs with the cationic surfactant TBDMAC at pH 10. However, even for this system, the lag time is approximately 30 minutes and so the time required for removal is long relative to that for untreated, liquid TAG mixture. Using the 43 mM TBDMAC/pH 10 system, we have investigated how the addition of various co-solvents or co-surfactants affect the removal. As seen in Figure 12, the addition of 1-10 vol% butanol strongly reduces the TAG film removal time with the 10 vol% butanol + surfactant system achieving faster TAG removal than pure butanol alone. The added butanol could enhance the cleaning performance in several different ways. It may (i) partition to the thermally aged TAG, soften it and thereby speed up surfactant partitioning to the TAG film; (ii) partition to the TAG and increase its affinity for the surfactant, i.e. increase K_{ow} and/or (iii) act as a co-surfactant to increase the TAG solubilisation in the mixed butanol-TBDMAC micelles. In separate experiments, we have measured that K_{ow} for TBDMAC partitioning into thermally aged TAG films at pH 10 and 40°C is increased from 4.6 to 6.3 by the addition of 10 vol% butanol to the aqueous phase. Hence, factor (ii) certainly contributes to the observed cleaning enhancement; the extent to which factors (i) and (iii) may contribute is currently unknown.

Figure 13 summarises the effects of many different additives on the thermally-aged TAG film removal. The logarithmic scale ordinate of the measured time required for 50% removal of the thermally aged TAG film provides a convenient measure of overall TAG removal rate. The “base system” of 43 mM TBDMAC at pH 10 removes 50% of the TAG film in approximately 105 minutes, as indicated by the horizontal dashed line. Some additives (butanol, pentanol, heptanol, decanol, hexadecanol and anisole) reduce the 50% removal time whereas others (methanol, dodec-1-ene, and chloroform) increase the time. In general, the removal enhancing additives (alcohols and anisole) possess an amphiphilic structure consisting a hydrophobic group joined to a hydrophilic group. They all have a co-surfactant character which is likely to increase TAG solubilisation in the aqueous micelles. As noted above, they may also act to soften the thermally aged TAG and increase its affinity for the surfactant, as seen in the increase in K_{ow} observed for butanol addition.

The additives which have a negative impact on the cleaning (i.e. they increase the 50% removal time) are of two types. Addition of the water miscible co-solvent methanol generally increases the cmc of surfactants[23]. Hence, methanol addition is expected to increase the cmc, reduce the concentration of micelles, reduce the TAG solubilisation capacity of the aqueous solution and thereby reduce the film removal rate, as seen here. The water-immiscible hydrophobic species chloroform and dodecene are dissolved in the aqueous phase by solubilisation within the hydrophobic cores of the micelles. Filling the micelles with these hydrophobic additives blocks the solubilisation of the TAG and hence reduces the cleaning effect.

Thermally-aged, semi-solid TAG deposits have generally been regarded as difficult to remove using aqueous surfactant solutions as the roll-up/emulsification or solubilisation mechanisms for the removal of liquid TAGs are not applicable. We have shown here that thermally-aged TAG film removal occurs in two steps. In the first, lag-phase step, the surfactant partitions from the aqueous solution to the TAG film. In the second step, the surfactant in the TAG phase self-assembles into micelles containing solubilised TAG and exits into the water phase, thereby removing the TAG film from the surface. Interestingly, surfactant partitioning to untreated, liquid TAG is low whereas partitioning to the semi-solid, thermally aged TAG films is much higher, probably as a result of the presence of the product species formed by reactions of the TAGs during thermal treatment. We have found the effectiveness of this TAG film removal process varies with pH in a manner that depends on the charge type of the surfactant used. Cationic surfactants require a high pH whereas anionic and non-ionic surfactants require low and intermediate pH values respectively. This conclusion has wide ranging implications for the design of thermally aged TAG film removal formulations required to operate under particular pH conditions. Finally, we have shown that amphiphilic additives, including amphiphilic perfume components such as anisole, can increase the speed of thermally-aged TAG film removal whereas additives which are either too hydrophilic or too hydrophobic reduce the speed of TAG removal.

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References

1. Raney KH, Benson HL (1990) The effect of polar soil components on the phase inversion temperature and optimum detergency conditions. J Am Oil Chem Soc 67:722-729
2. Miller CA, Raney KH (1993) Solubilization-emulsification mechanisms of detergency. Colloids & Surfaces A 74:169-215
3. Chen B-H, Miller CA, Garrett PR (1997) Rates of solubilisation of triolein into non-ionic surfactant solutions. Colloids & Surfaces A 128:129-143
4. Chen B-H, Miller CA (1998) Rates of solubilisation of triolein/fatty acid mixtures by non-ionic surfactant mixtures. Langmuir 14:31-41
5. Gotoh K (2005) The role of liquid penetration in detergency of long-chain fatty acid. J Surfact Deterg 8:305-310
6. Alameda EJ, Rodriguez VB, Olea JN, Moreno RB, Borrego AG, Vaz DA (2009) Design of experiments to evaluate the detergency of surfactants on fatty soils in a continuous-flow device. J Surfact Deterg 12:191-199
7. Alameda EJ, Rodriguez VB, Moreno RB, Olea JN, Vaz DA (2011) Fatty soils removal from hard surfaces in a clean-in-place system. J Food Proc Eng 34:1053-1070
8. Alameda EJ, Roman MG, Vaz, DA, Perez JLJ (2012), Assessment of the use of ozone for cleaning fatty soils in the food industry. J Food Eng 110:44-52

9. Gillam NW (1949) Variation of chemical reactions with temperature during the oxidation and polymerization of fatty oils. Aust Chem Inst J & Proc Jan:19-36
10. Lewis WR, Quackenbush FW (1949) The use of the polarograph to distinguish between the peroxide structures in oxidised fats. J Am Oil Chem Soc 26:53-57
11. Hess PS, O'Hare GA (1950) Oxidation of linseed oil: temperature effects. Ind Eng Chem 42:1424-1431
12. Johnson OC, Kummerow FA (1957) Chemical changes which take place in an edible oil during thermal oxidation. J Am Oil Chem Soc 34:407-409
13. Blumenthal MM (1991) A new look at the chemistry and physics of deep-fat frying. Food Technol Feb:68-71
14. Muizbelt WJ, Nielen MWF (1996) Oxidative crosslinking of unsaturated fatty acids studied with mass spectrometry. J Mass Spec 31:545-554
15. Tan CP, Che Man YB (1999) Differential scanning calorimetric analysis for monitoring the oxidation of heated oils. Food Chem 67:177-184
16. Tan CP, Che Man YB (1999) Quantitative differential scanning calorimetric analysis for determining total polar compounds in heated oils. J Am Oil Chem Soc 76:1047-1057
17. Choe E, Min DB (2007) Chemistry of deep-fat frying oils. J Food Sci 72:R77-R86
18. Kalogianni EP, Karapantsios TD, Miller R (2011) Effect of repeated frying on the viscosity, density and dynamic interfacial tension of palm and olive oil. J Food Eng 105:169-179
19. Hilditch T, Williams P (1964) The Chemical Constitution of Natural Fats, 4th Edn. Chapman and Hall, London
20. Reid VW, Longman GF, Heinerth E (1967) Determination of anionic-active detergents by two-phase titration. Tenside 9:292-304
21. Tsubouchi M, Tanaka Y (1984) Determination of poly(oxyethylene) non-ionic surfactants by two-phase titration. Talanta 31:633-634
22. Salama IE (2011) Surfactant properties of corrosion inhibitors. PhD thesis, University of Hull, UK
23. Mukherjee P, Mysels KJ (1971) Critical micelle concentration os aqueous surfactant solutions. Nat Stand Ref Data Ser Nat Bur Stand, Washington DC
24. Guthrie JP (1978) Hydrolysis of esters of oxy acids: pKa values for strong acids; Bronsted relationship for attack of water at methyl; free energies of hydrolysis of esters of oxy acids; and a linear relationship between free energy of hydrolysis and pKa holding over a range of 20 pK units. Can J Chem 56:2342-2354

Table 1. *Composition of the untreated TAG mixture expressed as the wt% of fatty acids contained in the mixture of triglyceride oils (derived from information in ref. 19).*

no. carbons	***no. double bonds***	***wt% in ASTM grease***
14	0	0.3
16	0	14.5
18	0	5.8
20	0	0.3
22	0	0.3
24	0	0.3
16	1	1.0
18	1	31.5
18	2	22.3
18	3	5.1
20	1	1.3
22	1	17.2

Table 2. *Iodine values of ASTM grease samples subjected to different thermal treatment times and temperatures.*

Thermal treatment time / hrs	***Temperature / °C***	***Iodine value***
0	-	47.1 ± 0.4
1	150	47.3 ± 0.6
2	150	47.2 ± 0.8
3	150	47.7 ± 0.5
1	200	21.1 ± 0.3
2	200	21.1 ± 0.6
3	200	21.6 ± 0.5
1	250	21.3 ± 0.7
2	250	21.7 ± 0.6
3	250	21.2 ± 0.4

Table 3. *Critical micelle concentration (cmc) values at 40^{o}C for the surfactant solutions used here. The electrolyte compositions of the different pH solutions are noted in the text. TBDMAC value was interpolated from values in ref. 22. SDS value refers to 100 mM NaCl at 40^{o}C, from ref. 23. SOS values were measured in this work. C10E6 value refers to water at 40^{o}C, from ref. 23.*

surfactant	***pH***	***cmc/mM***
TBDMAC	1, 4, 7 and 10	Approx. 1
(cationic)		
SDS	1, 4, 7 and 10	Approx. 1.6
(anionic)		
SOS	1	26
(anionic)	4	43
	7	47
	10	36
C10E6	1, 4, 7 and 10	Approx. 0.7
(non-ionic)		

Figure 1. DSC heating and cooling curves for untreated and thermally aged (heated on a glass slide for 1 hour at 200°C) TAG mixture samples. The plots correspond to the second cycle of heating to 90°C, holding at 90°C for 5 minutes and cooling to -20°C with a heating/cooling rate of 5°C/minute.

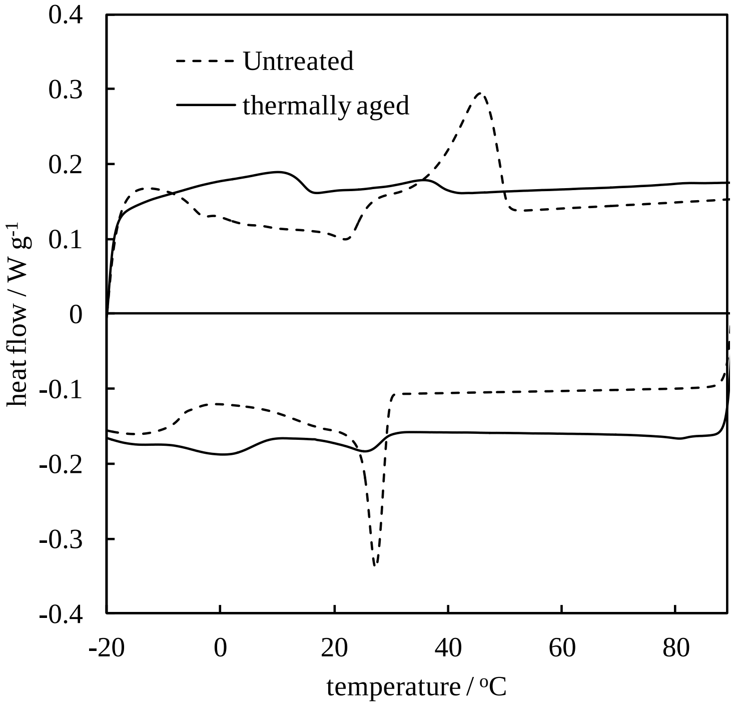


Figure 2. Effect of different thermal treatment conditions on thermally aged TAG film removal using 250 ml of 43 mM TBDMAC (cationic) surfactant solution, pH 10 at 40^{o}C.

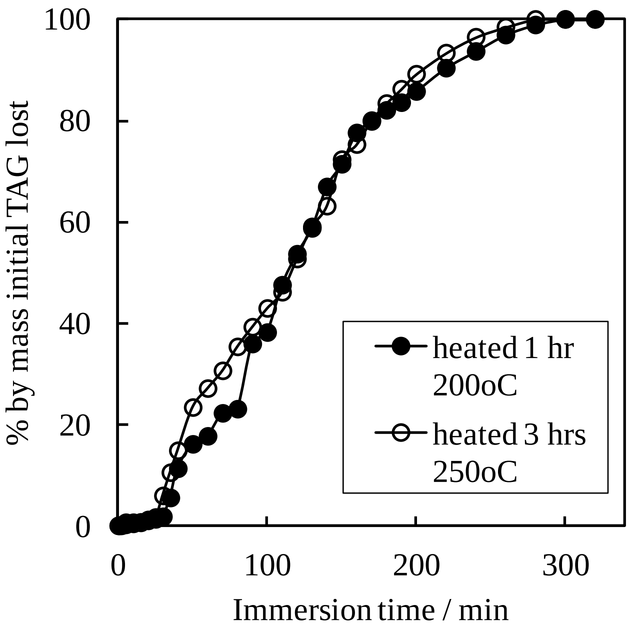


Figure 3. Effect of initial mass of the TAG films (thermally aged for 1 hour at 200°C) on their removal using 250 ml of 43 mM TBDMAC (cationic) surfactant solution at 40°C. The initial TAG film thicknesses (in order of increasing mass) are 140, 215 and 398 μm.

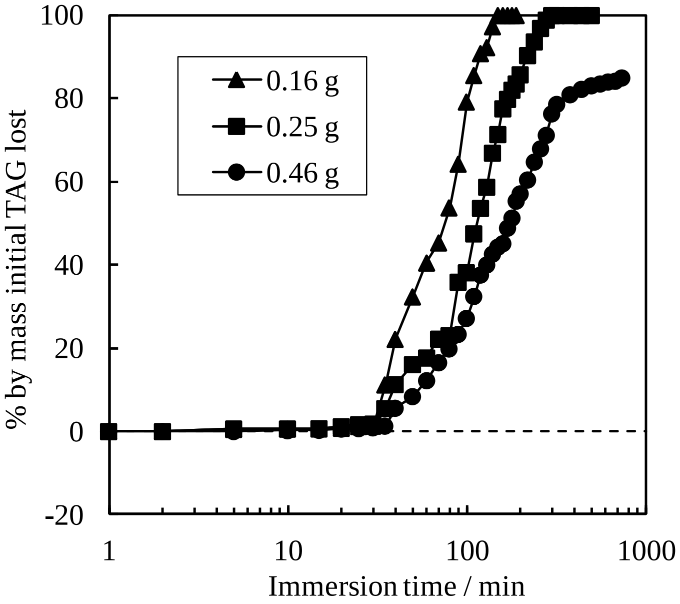


Figure 4. Thermally-aged TAG film mass loss versus time for different concentrations of TBDMAC (cationic) surfactant (250 ml) at pH 10 and 40^{o}C. The horizontal dashed lines indicate the total initial mass of TAG mixture for each experiment.

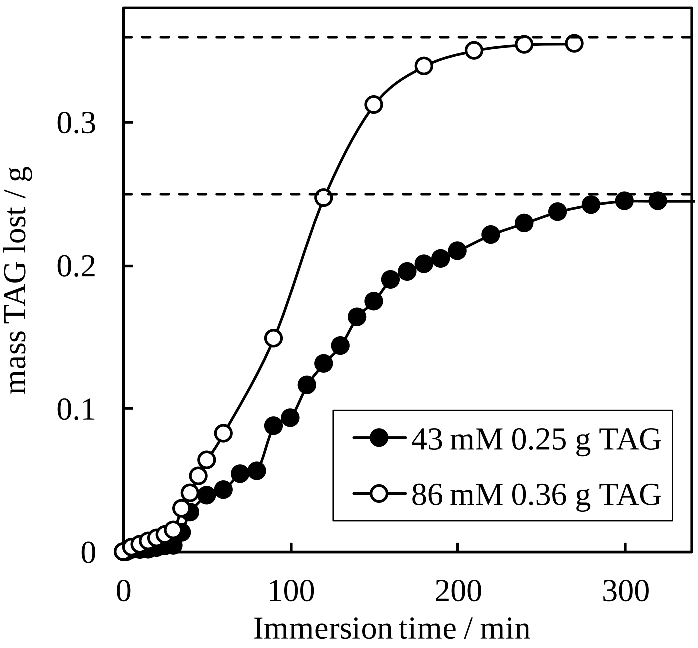
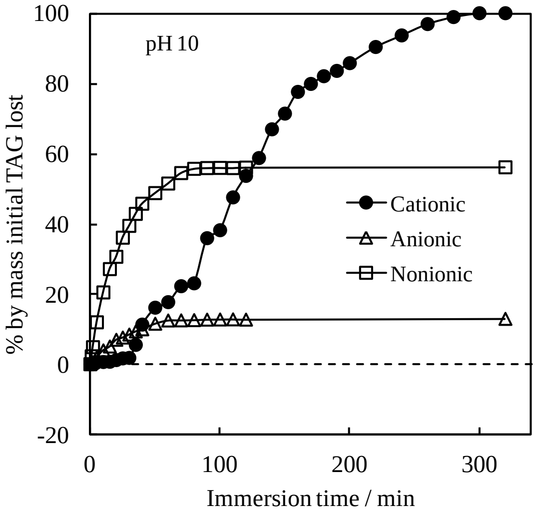
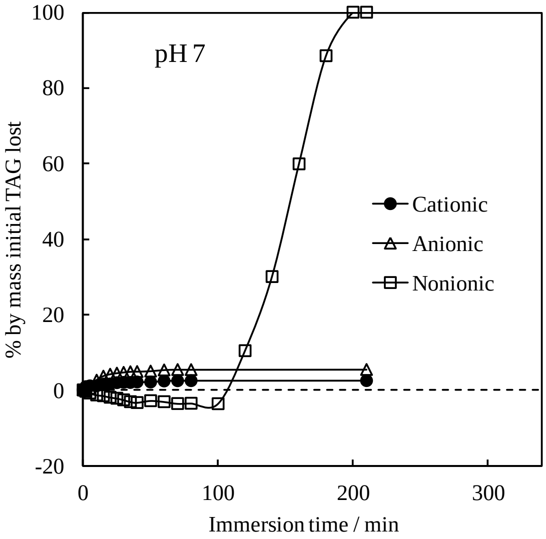
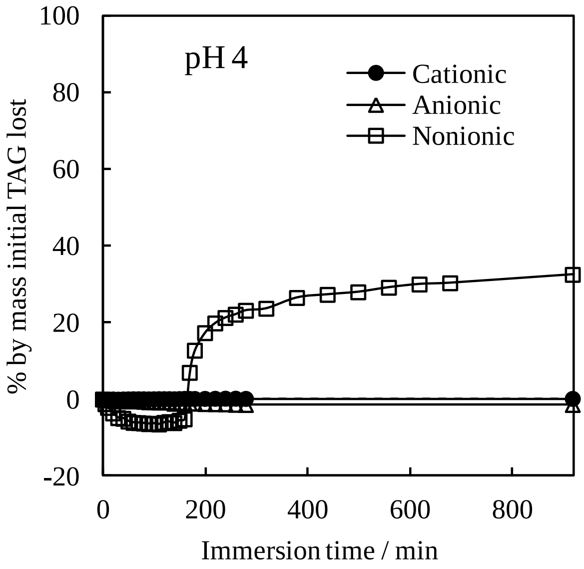


Figure 5. Effects of pH and surfactant charge type on the removal of TAG films (thermally aged for 1 hour at 200°C) using 250 ml of 43 mM surfactant solutions at 40°C. For the surfactants, the cationic is TBDMAC, non-ionic is C10E6 and the anionic is SOS.






pH 4
Cationic
Anionic
Nonionic
% by mass initial TAG lost
100
80
60
40
20
0
-20
0
200
400
600
800
Immersion time / min

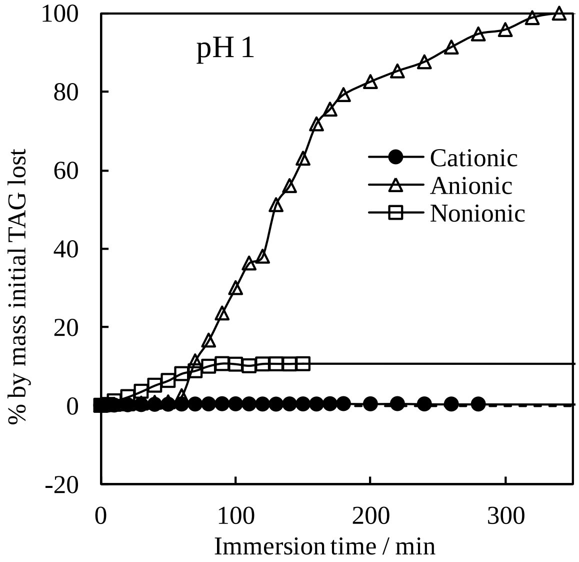

pH 1
Cationic
Anionic
Nonionic
% by mass initial TAG lost
100
80
60
40
20
0
-20
0
100
200
300
Immersion time / min

Figure 6. Effect of pH on the maximum mass of thermally aged TAG mixture which can be solubilised into 250 ml of 43 mM solutions of the different surfactants at 40°C. The horizontal dashed line shows the typical mass of TAG used in the TAG film removal experiments; 100% TAG film removal is only observed when the maximum solubilisation exceeds this value.

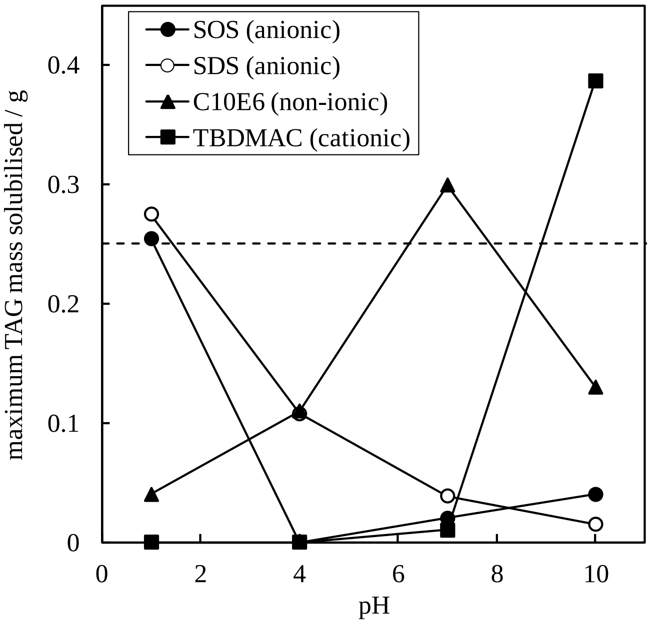


Figure 7. Effect of temperature on the removal of TAG films (thermally aged for 1 hour at 200^{o}C) using 250 ml of 43 mM TBDMAC (cationic) surfactant solution at pH 10.

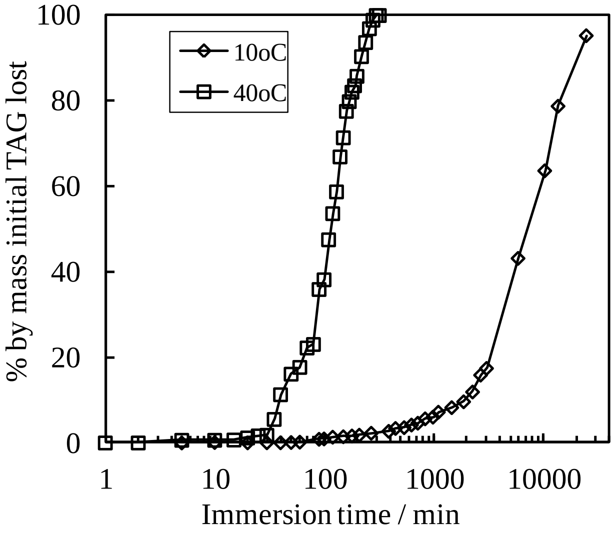


Figure 8. SEM images of thermally aged TAG films. Top image: TAG film before immersion in surfactant solution. Middle image: film after immersion in 43 mM cationic TBDMAC solution at pH 10 and 40°C for 50 minutes (corresponding to approximately 10% TAG removed). Bottom image: film after immersion in 43 mM non-ionic C10E6 solution at pH 7 and 40°C for 80 minutes (corresponding to 5% mass *gain* of the TAG film).

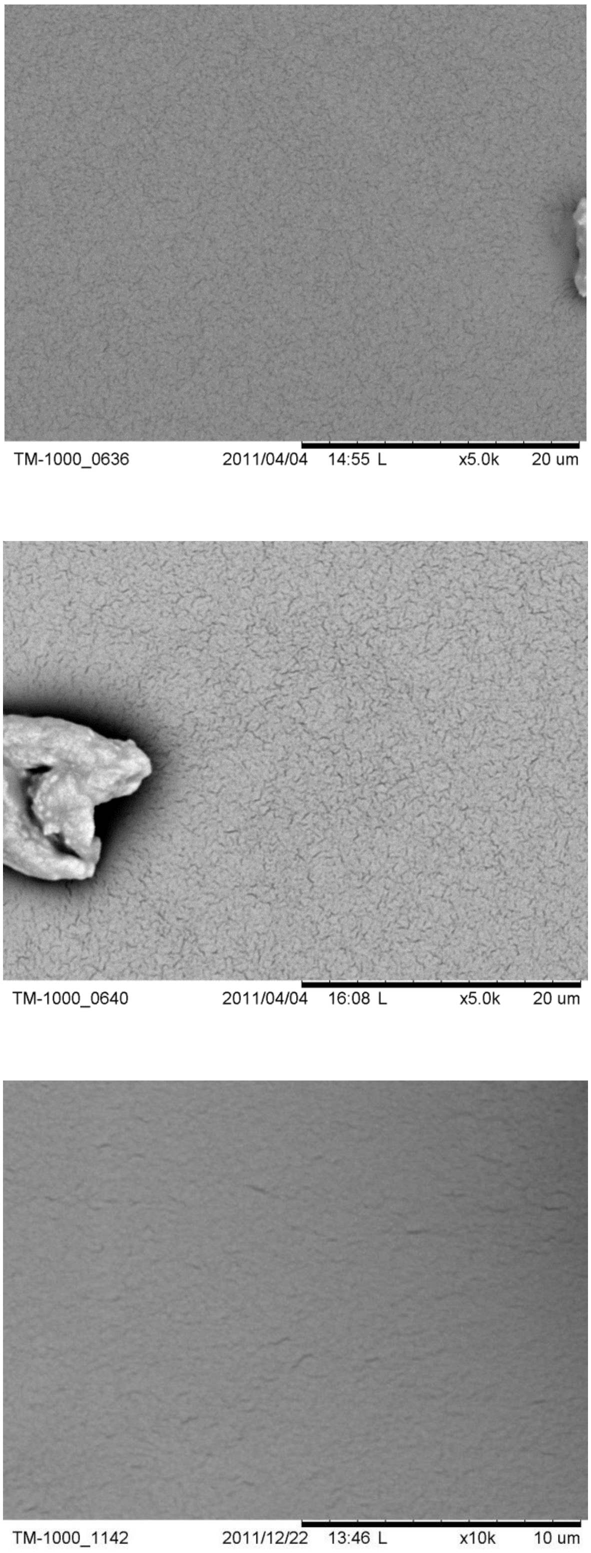


Figure 9. Variation with time of the surfactant concentration in the thermally aged TAG films (0.25 g thermally aged for 1 hour at 200°C) for the cationic (TBDMAC) and anionic (SOS) surfactants at pH 1 and 10 following immersion in 50 ml of 43 mM surfactant solution at 40°C.

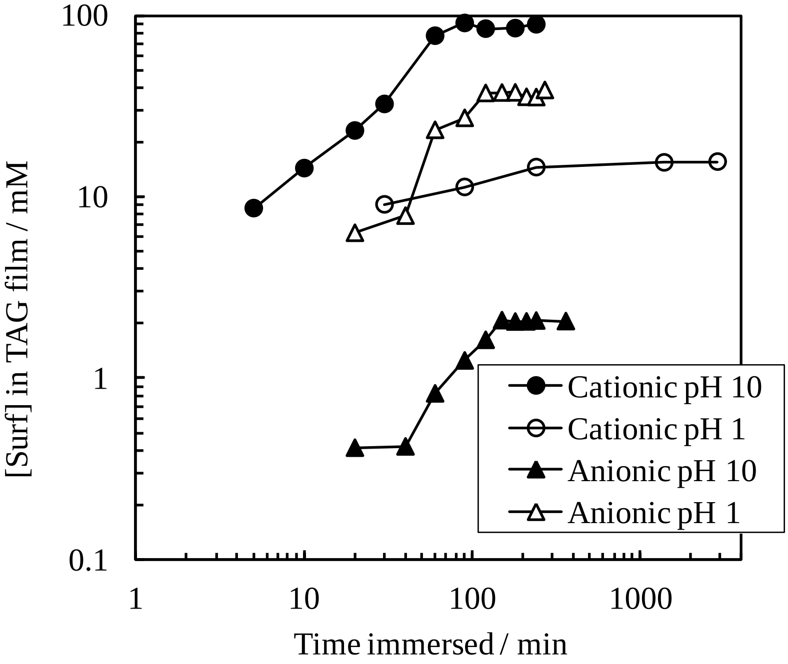


Figure 10. Variation of TAG-water partition coefficient (K_{ow}) with pH for the different surfactants into thermally aged TAG (upper plot) and untreated TAG (lower plot).

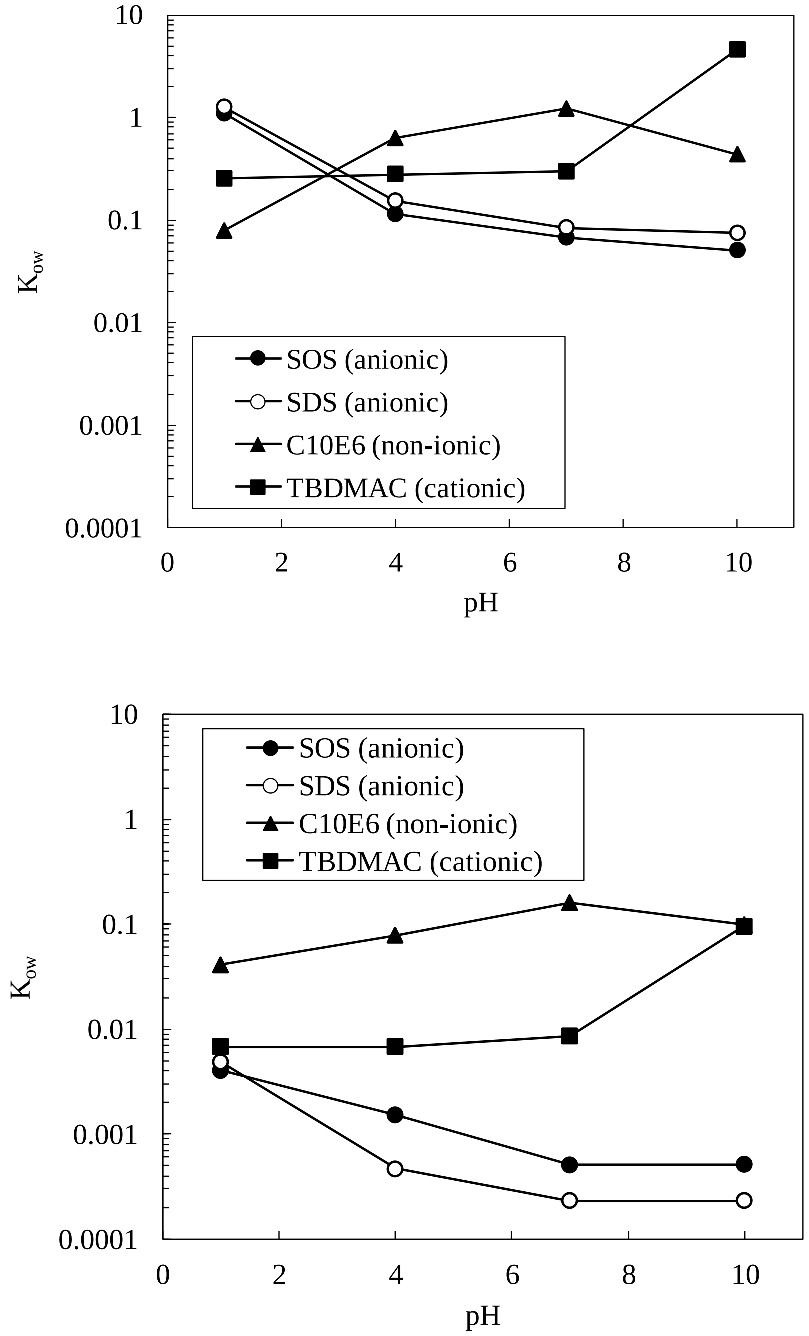


Figure 11. Percentage mass loss versus time for thermally-aged TAG films with and without pre-doping with 10 mM TBDMAC (cationic) surfactant. The aqueous solution volume was 250 ml and the temperature was 40°C in each case.

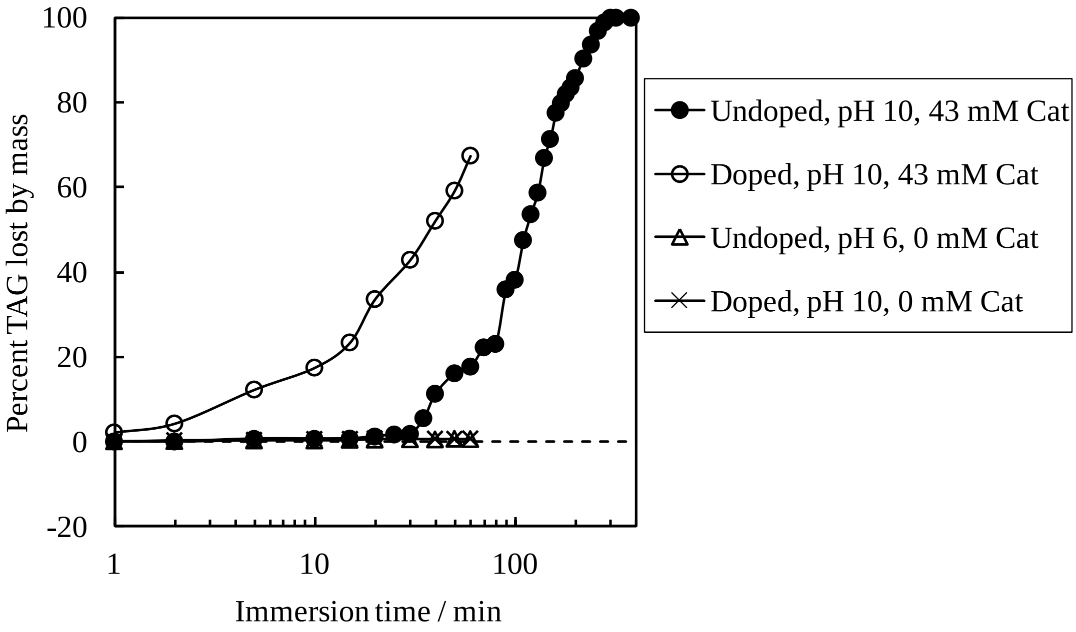


Figure 12. Percentage mass loss versus time for thermally-aged TAG films in solutions containing 43 mM TBDMAC (cationic) surfactant and different concentrations of 1-butanol. The aqueous solution volume was 250 ml, pH = 10 and the temperature was 40°C in each case.

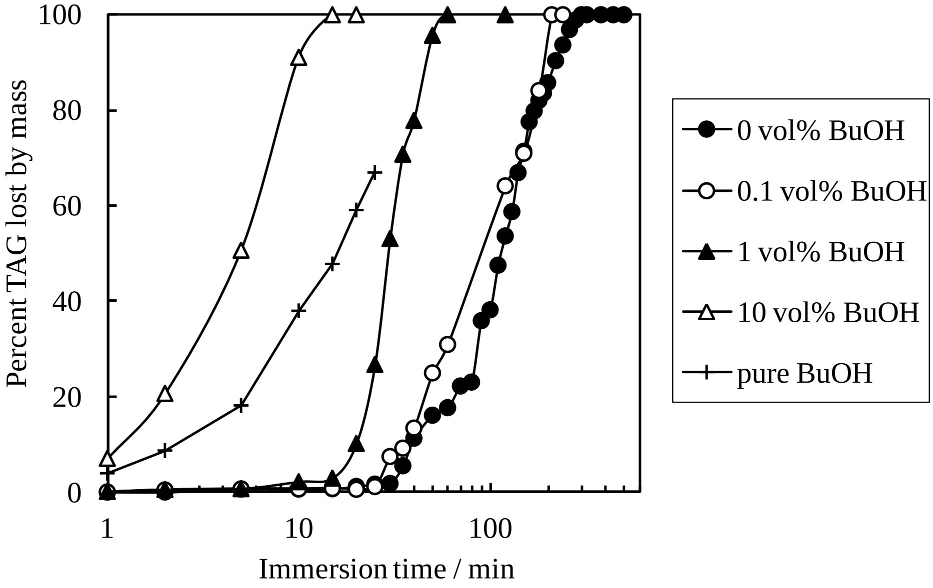


Figure 13. Immersion time required to achieve 50% TAG film removal at 40^{o}C in 250 ml solutions containing 43 mM cationic surfactant plus different additives at pH = 10 and 40^{o}C. The horizontal dashed line shows the time for 50% removal in the absence of additive.