Experimental Report

Proposal: **9-12-342** **Council:** 10/2012

Title: Anomalous gelation of engine oil

This proposal is resubmission of: 9-12-321

Research Area: Chemistry

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Samples: $CaCO_3$ particles in dodecane stabilised with a salicylate surfactant

Instrument	Req. Days	All. Days	From	To
D33	2	2	01/05/2013	03/05/2013

Abstract:

Engine oil contains 1 - 10 nm calcium carbonate particles stabilised with a surfactant. One commonly used surfactant headgroup is salicylate and we have shown that in the presence of moisture these surfactants are stripped from the particle surface, resulting in aggregation. We have observed that when using a magnesum cation for the salicylate headgroup the resulting dispersion gels, in the presence of moisture. We wish to understand this process.

We have shown that the salicylate surfactant in organic solvent forms a number of different morphologies dependent on the cation and we hypothesise that these different shapes result in differing depletion interaction and hence differing dispersion behaviour.

Using SANS we will determine the particle structure in the gel and also investigate the dynamics of formation. Combined with rheological data this work will show the range and magnitude of the attractive potential leading to gelation.

Experiment proposal number 9-12-342

Anomalous gelation of engine oil

Introduction

Nanoparticles of metal carbonate are added to engine oil to neutralise acids. Surfactants are adsorbed to the surface of these particles during their preparation and are essential to ensuring stability, acting as a steric barrier to aggregation. Contamination of the lubricant with water and other polar molecules can negatively affect the stability and effectiveness of this class of additive.[1] Increased use of biodeisel is exacerbating this issue, making the study of these additives ever more important.

Particularly interesting is the effect of the surfactant metal counter-ion, which determines the additive's response to water contamination. On addition of water to solutions of calcium alkyl salicylate stabilised particles in dodecane, partial aggregation is observed. This can be explained by the partial removal of the steric stabilisation layer of surfactant molecules, causing destabilisation. However, when the same proportion of water is added to the equivalent magnesium particle system, gelling of the sample occurs over the subsequent days or weeks. A previous study has shown that different shape inverse micelles of these surfactants form in wet and dry non-aqueous solvents, depending on the counter-ion.[2]

The aim of this work is to measure the gelling system using small angle neutron scattering to learn the mechanism for gelation and the interactions causing the arrest. Understanding the interactions of the water with the surfactants and overbased detergents will aid the design of additives to mitigate these negative effects.

Materials and methods

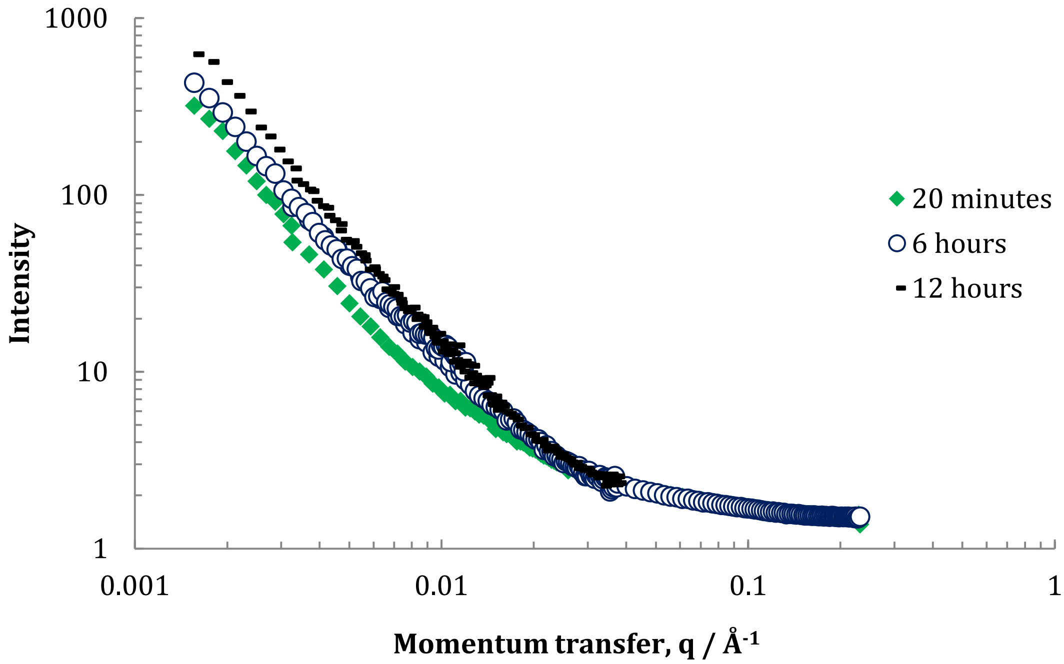
The engine oil additives studied were kindly provided by Infineum UK and were used with no further purification. Samples were studied at ambient temperature on D33 using a sample changer. Three detector configurations were used, allowing a total q range of 0.0016 – 0.23 $Å^{-1}$.

Results and analysis

SANS measurements of the dry particles prior to aggregation gave a radius of 23 Å, with the surfactant sheath measured to be 9 Å.

Measurements were taken on samples both that had been gelled for a long period of time (30 days) and those in the initial stages, i.e. measurements commenced just after water was added. In these samples a clear increase in the scattering at lower q is observed with time (see figure 1 and 2). Small angle scattering has often been used to study aggregation phenomena.[3] Measurement of the structure factor over the range $R_G^{-1} \leq q \leq a^{-1}$, where R_G is the radius of gyration of the cluster of particles and a is the particle radius, allows determination of the fractal dimension, D. The fractal dimension is the gradient of the power-law decay observed in $S(q)$,[4]

$S(q) \sim q^{-D}$.



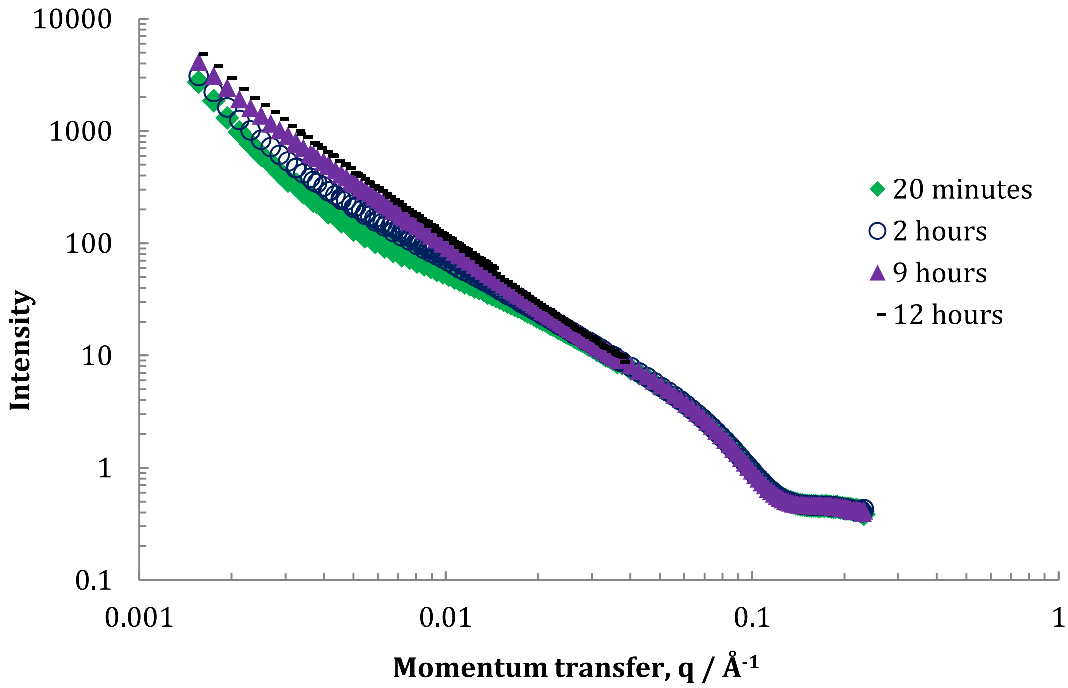


Figure 1. Scattering curves obtained at different times after water was added to solutions of overbased detergent particles. The two graphs show scattering from samples of differently contrasted solutions.

The fractal dimension is a description of how dense the aggregate is, which in turn can be used to infer an aggregation mechanism. For this gelling system it was found that D = 2.0, when calculated from the measurement taken after 12 hours. In a review article of light scattering by fractal aggregates, it is stated that the fractal dimension expected with diffusion limited cluster aggregation, DLCA, is D = 1.75 to 1.8. In the case of reaction limited cluster aggregation, then D = 2.1 to 2.2 is expected.[3] The value found for this system clearly lies in between these two regimes. This could be due to rearrangement of the clusters during aggregation, which is not accounted for by these aggregation mechanisms.

Change in the structure of the aggregates formed by the salicylate surfactant molecules when in wet and dry oils is intriguing.[2] The shape and size of the aggregates formed by the magnesium salicylate in wetted dodecane open the possibility of a depletion interaction. This interaction could be on a lengthscale greater than that of the steric stabilisation in the particle-particle potential, leading to a secondary minimum. It would be interesting to investigate the effect of changing the concentration of surfactant on the scattering, and the fractal dimension of the gel formed.

References

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(2) Lee, C. L.; Dowding, P. J.; Doyle, A. R.; Bakker, K. M.; Lam, S. S.; Rogers, S. E.; Routh, A. F. *Langmuir* **2013**, *29*, 14763.

(3) Sorensen, C. M. *Aerosol Sci. Technol.* **2001**, *35*, 648.

(4) Schaefer, D. W.; Martin, J. E.; Wiltzius, P.; Cannell, D. S. *Phys. Rev. Lett.* **1984**, *52*, 2371.