Experimental report

14/05/2017

Proposal:	**1-04-98**	**Council:**	4/2015
Title:	Characterisation of pre-nucleation structures and subsequent crystal growth/ phase transition processes for C16/C18 alkanes used in biofuels		
Research area:	Chemistry		

This proposal is a new proposal

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Samples:
h-toluene
d-Hexadecane
n-dodecane
d-dodecane
d-toleune
n-hexadecane
n-octadecane
d-octadecane

Instrument	Requested days	Allocated days	From	To
D22	2	0		
D11	2	2	01/06/2016	03/06/2016
D33	2	0		

Abstract:

Environmental concerns have led to increasing use of sustainable, bio-derived feedstocks in fuels including hydrogenated vegetable oil (consisting of C16 and C18 alkane components). Poor fuel quality can result in vehicle failures due a lack of understanding of diesel crystallisation. In particular, the initial stage of crystallisation, involving nucleation of molecules to form molecular clusters from a supersaturated solution is not fully understood.

The proposed experiment will probe the structural evolution of single molecules (through dynamic evolution of the nuclei structure, such as shape and size, as a function of supersaturation) to molecular clusters through to nano-sized crystallites.

The results will complement previous x-ray studies and allow accurate determination of form factors in and allow determination of prenucleation structures. This will help build a structural picture of a nucleation event, allowing elucidation of the thermodynamics and kinetics associated with solute molecule aggregation to form crystalline phases and the effect on crystal properties. The study will assist in understanding biofuel crystallisation and ways to improve cold-flow properties.

Characterisation of pre-nucleation/ crystal structures for C16/C18 alkanes used in biofuels

Introduction

Increased levels of biofuel are leading to vehicle failures which are a result of poor understanding of biofuel crystallisation. Biofuel molecules include hydrogenated vegetable oil (HVO) from agricultural or recycled sources which consist mainly of C16 and C18 alkane components [1].Understanding such mechanistic information could provide a step towards the directed assembly of molecules for the design of crystallisation processes.

DSC measurements in combination with powder X-ray diffraction, performed on binary mixtures of C16/C18 identified the presence of a rotation phase (R_1, F_{mmm}) from high temperature region. The aim of the SANS experiment was discover the effect of rotator phase formation and solvent environment on the crystallisation mechanism for mixtures of C16/C18.

Methodology

Three compositions of C16/18 mixtures were chosen to be the solute samples which are pure C16, equimolar of C16/C18 and pure C18. Representative fuel solvents of toluene and kerosene were employed. The solute and solvent chemicals were prepared in solution with contrast variations from different deuteration samples (Table 1). The solutions were heated to 5°C above saturation temperature in a sealed laboratory bottle with a screw cap in a pre-heated oven.

Table 1. Concentrations and specific solute and solvents for systems studied

Sample No.	Conc. (w/w %)	Con. (g/l)	Solute	Solvent
2	49	846	h-0.5C16/ h-0.5C18	d-Toluene
3	51	846	d-C16	Kerosene
4	51	846	d-0.5C16/ d-0.5C18	Kerosene
5	51	846	d-0.5C16/ h-0.5C18	Kerosene
6	51	846	h-0.5C16/ d-0.5C18	Kerosene
7	51	846	d-C16	Kerosene
8	49	846	h-C16	d-Toluene
9	51	846	d-C18	Kerosene
10	49	846	h-C18	d-Toluene
11	49	846	h-0.5C16/ d-0.5C18	d-Toluene
12	49	846	d-0.5C16/ h-0.5C18	d-Toluene

Results

Figure 1 Time-resolved plots of absolute intensity of I(Q) versus the merged Q range from HQ to LQ for equimolar mixed C16/C18 (S5) during cooling in kerosene solution. The temperature range is from 280K to 274K. The flat plots at 280K and 278.5K correspond to the background of homogeneous mixed of solute and solvent monomers. At 277K the total scattering intensity increases markedly with a curve slope in the Q region (Q_{max}=0.0045 Å) owing to C16/C18 aggregates formation in solution prior to crystallisation. This intermediate structure subsequently grows into large clusters towards to lower Q at 275.5K. The curve shape kept steady in the lower Q range with slightly increasing of scattering intensity at 274K.

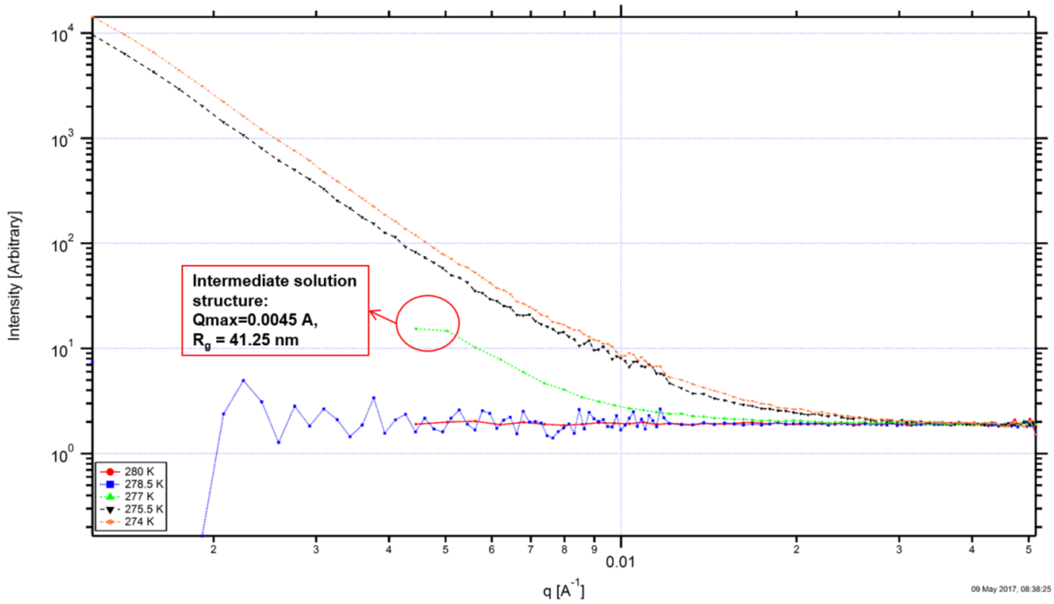

Figure 1 Scattering intensity for a cooling crystallisation at set isothermal temperature points of 280, 278.5, 277, 275.5 and 274 K, indicating an observed Q_{max} region of slope changes at 277K relating to a molecular cluster in the solution prior to crystallisation.

The unified fit method in the program Irena was used [2] to model Gunier and power law fitting in order to obtain the size (R_g) and fractal dimensionality (P) Generally, for surface fractals 3 < P <4, for mass fractals P < 3 and for diffuse interfaces P > 4. Values of R_g and P in both HQ and LQ regions for the sample of **S5** at three isothermal temperatures during cooling are shown in **table 2**. Since the single molecule of the solid solution (R_1) of C16/C18 mixture has a c-axis length around 4.8 nm. The progression increase of Rg values from 4.85 to 16.7 nm in HQ can be correlated to the monomers of solid solution rotator phase of C16/C18 mixture growing to larger group i.e. dimer or trimer molecules. The corresponding P values of these molecular structures interpreted the low ordering fractal properties for mass fractals P < 3. The subsequently grown aggregates were detected with R_g value of 41.25 nm of the intermediate structure in solution. The terminal large cluster with R_g values around 170 nm and high ordering fractal with surface fractals from the mass fractal of intermediate aggregates.

Table 2 Power law value (P) and Rg (nm) during crystallisation obtained from Unified fit analysis of S5 collected at three isothermal temperatures during cooling

		HQ		LQ	
Tem (K)	**Tem (C)**	**Rg**	**Power law**	**Rg**	**Power law**
277	3.85	4.85	1.41	41.3	2.54
275.5	2.35	16.73	1.34	177.2	3.37
274	0.85	12.72	1.00	169.7	3.24

This transformation process from monomers to intermediate aggregates and to the terminal large clusters was only observable in S5. Reasons can be due to the deuteration solutes as it was not seen from S6 where C18 was deuterated rather than C16. Large clusters were detected from mixture samples of S12 and S3, the size and P values observed from Unified fit are given in **Table 3**.

Table 3 Power law value (P) and Rg (nm) during crystallisation obtained from Unified fit analysis of S12 and S2.

		HQ		LQ	
Sample	**Tem (K)**	**Rg**	**Power law**	**Rg**	**Power law**
S12	273.5	12.74	1	151.7	3.61
S2	272.18	48.58	3.70	138.88	3.45

C18 or C16 crystallising from kerosene and toluene solutions were found with large cluster formation. However, no intermediate aggregates were detectable (**Figure 3**). This can be due to the pathway of triclinic phase crystallisation differed from the mixture R_1 phase. Nucleation mechanism was expected as instantaneous nucleation. Resolved cluster sizes were found to be smaller in toluene solvent and for a solute of shorter chain length (C16) (**Table 4**).

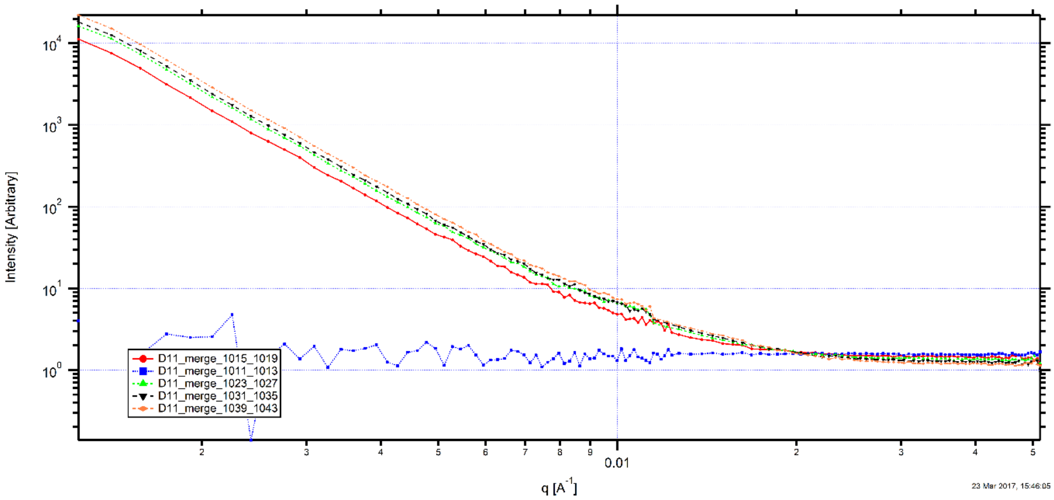

Table 4 Power law value (P) and Rg (nm) during crystallisation obtained from Unified fit analysis of S9 at three iso-temperatures

			HQ		LQ	
Sample	**Tem (K)**	**Tem (C)**	**Rg**	**Power law**	**Rg**	**Power law**
S9 (d-C18 in Kerosene)	282	8.85	6.54	2.19	169.69	3.24
	279.8	6.65	10.02	3.00	160.08	3.76
	277	3.85	6.77	1.71	179.63	3.92
S10 (C18 in d-Toluene)	282	8.85	5.11	1.46	160.61	4.24
	272.9	-0.25	5.89	1.80	163.04	4
S7 (C16 in d-Toluene)	274	0.85	0.3	1	131.87	2.61

References

1. Schenk, P.M., et al., *Second generation biofuels: high-efficiency microalgae for biodiesel production.* Bioenergy research, 2008. **1**(1): p. 20-43.
2. Ilavsky, J. and P.R. Jemian, *Irena: tool suite for modeling and analysis of small-angle scattering.* Journal of Applied Crystallography, 2009. **42**(2): p. 347-353.