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BEHAVIOUR OF WATER IN AVIATION FUELS AT LOW TEMPERATURES

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Abstract

The presence of water in aviation fuel has been a topic of concern for the aviation industry for many decades since any contaminating water may freeze during long flights at high altitudes creating fuel flow problems. The aim of the present work was to improve the fundamental understanding of the behaviour of water in aviation fuel at the low temperatures experienced during flight.

Water droplet and ice formation were studied at temperatures down to -60°C in jet fuels representative of 100% Merox, 100% hydroprocessed and commercially-supplied Jet A-1 fuels. Parallel studies were carried out in model hydrocarbons representing the aromatic, cyclic and alkane components of jet fuel.

The dependence of water droplet and ice particle size was investigated as a function of parameters such as initial water concentration, rate of cooling, fuel composition and hydrocarbon type, and the presence of additives and impurities.

Initial studies using low temperature microscopy and particle size analysis indicated that, as the fuel cools, water is released in very fine droplets of size 5µm and below. On cooling the fuel to -44°C the droplets appear to remain and there was no indication of ice crystal structures being formed. Differential Scanning Calorimetry indicated that the water droplets were supercooling to temperatures as low as -40°C. The factors affecting droplet formation are discussed.

Keywords Aviation fuel, Jet A-1, aromatic hydrocarbons, low temperatures, water, ice, DSC, cold stage

1. Introduction

Water can dissolve in aviation fuel or be present as free water. Its presence is of concern to the aviation industry since free water may freeze over the course of a long flight at altitude and the resulting ice particles could block fuel filters or otherwise interfere with the steady flow of fuel to aircraft engines. The mechanism of water uptake, water shedding, droplet formation and the subsequent formation of ice is not well understood. It is a complex problem demanding an understanding of the solubility of water in jet fuel, nucleation and growth of water droplets, ice nucleation and growth, and the influence of fuel composition and fuel additives. The aim of the present work is to add to the understanding of these phenomena.

Hydroprocessed and Merox treated jet fuels can differ in some of their properties such as water retention and water shedding due to the difference in their chemical composition resulting from their different treatment in the refinery. Hydroprocessing removes the sulphur and many of the polar impurities from the fuel, which may act as surfactants. The Merox process 'wraps up' the sulphur within the hydrocarbon molecules converting it to a less reactive form; it does not reduce the total amount of sulphur nor the natural impurities or surfactants which come from the original crude oil. A typical Jet A-1 will contain a mixture of hydroprocessed and Merox treated fuel.

All conventional jet fuels consist wholly of hydrocarbons which are a mixture of straight chain, branched chain, cyclic and aromatic compounds. The hydrocarbon compounds will have between 8 and 16 carbon atoms, with the highest proportion having 12 carbon atoms. The only limit on the hydrocarbon composition of jet fuel is a maximum permitted value of 25% by volume of aromatic species.

Aromatic hydrocarbons have been found to have a greater solubility in water than other hydrocarbon structures with similar numbers of carbon atoms¹. There is also some evidence that water may dissolve in higher concentrations in aromatic compounds than in alkane or cyclic compounds of similar molecular mass. It is possible that fuels with a high aromatic content will tend to have a higher concentration of dissolved water. New synthetic fuels can have a very low aromatic content and therefore could show different water handling characteristics from conventional jet fuel.

By gaining a more fundamental understanding of water dropout and ice formation in model hydrocarbons and jet fuels over the temperature range experienced in aircraft flight, it is possible that a methodology can be developed to assist with the problem of water management in aviation fuels.

2. Fuels and Model Hydrocarbons used in this Study

By its nature, jet fuel is a bulk-supplied product and it is difficult to acquire small quantities of fuels, of known provenance, for research purposes; however, a major UK oil refiner agreed to supply two types of jet fuel which represented processing extremes for conventional fuels. A third fuel was supplied from an operating UK airfield:

- (i) 100% Merox treated jet fuel
- (ii) 100% hydroprocessed jet fuel
- (iii) Airfield Jet A-1.

The aromatics content of the hydroprocessed fuel was reported as 21.8% and the Merox fuel as 16.6%; the aromatics content of the airfield fuel was not reported since it was a blend from two batches of fuel. The fuels were supplied against the Jet A-1 specification. The first two fuels were not ideally fresh, being approximately one year old at the time of supply, but were essentially within specification. Using 'old' fuel is not ideal but, as has been noted, there are significant difficulties with supply of research quantities of Jet A-1.

The model hydrocarbons included in the study were:

- (i) N-octane to represent straight chain hydrocarbons
- (ii) Methylcyclohexane, to represent cyclic hydrocarbons
- (iii) Toluene, to represent aromatic hydrocarbons

All the hydrocarbons were AnalaR or HPLC grade.

The hydrocarbons chosen have a similar number of carbon atoms in their respective molecules. Various selection parameters were used, but the melting point was the most critical, followed by safety concerns over materials with low flashpoints. Some data on water solubility in various hydrocarbons has been reported^{2,3,4,5,6}.

3. Control and Measurement of Dissolved Water Concentration

It is well documented that the dissolved water content of fuels and hydrocarbons will change with temperature⁷ and relative humidity⁸. For consistency, it was deemed necessary to develop a procedure to prepare samples with reproducible concentrations of dissolved water. The fuel or hydrocarbon was contained in a glass beaker within a desiccator and a few ml of distilled water was added to the bottom of the desiccator so that water was always present to maintain 100% relative humidity. The desiccator was held at 25°C in a controlled temperature chamber and the fuel was stirred using a magnetic stirrer; the assembly was conditioned for a minimum of 24 hours. Samples were withdrawn by glass syringe and fine needle through a septum fitted to the desiccator, to avoid disturbing the equilibrium of the system.

This ‘conditioning’ procedure was used to produce hydrocarbon and fuels samples with repeatable (saturated) water content for the experimental programme.

Water concentrations were determined using a Metrohm 684 Karl Fischer Coulometer. This system uses a coulometric titration technique to measure both the dissolved and free water, and so gives the total water in a sample. Typically, ten measurements of water content were made for each sample and sample condition; data shown in the tables is the average of these measurements and also gives the degree of scatter.

3.1 Dissolved Water in Model Hydrocarbons

The dissolved water content of the three model hydrocarbons was measured by the Karl Fischer method for ‘as-received’ and ‘conditioned’ samples. The results shown in Table 1 indicate that for hydrocarbons of similar number of carbon atoms, the aromatic compound dissolved seven times more water than the alkane or cyclic compounds. At saturation, the cyclic hydrocarbon dissolved the least amount of water although the difference between it and the alkane was small.

Table 1 Concentration of dissolved water in model hydrocarbons

‘As-Received’		‘Conditioned’	
New bottle, ambient temperature ~25°C	Dissolved water ppm [by mass]	25°C, 100% relative humidity, for minimum of 24 hours, stirred	Dissolved water ppm [by mass]
N-octane	20 ±2	n-octane	80 ±2
Methylcyclohexane	29 ±2	Methylcyclohexane	74 ±2
Toluene	78 ±3	Toluene	566 ±10

3.2 Dissolved Water in Fuels

The dissolved water content of the three fuels, was measured by the Karl Fischer method for ‘as-received’ and ‘conditioned’ samples. As can be seen in Table 2, there was no significant difference between the three fuels. ‘Conditioned’ (saturated) fuels showed dissolved water content that had increased by more than two-fold, but again there was no statistically significant difference between the fuels.

Table 2 Concentration of dissolved water in fuels

‘As-Received’		
Sample	Storage Condition	Dissolved Water ppm [by mass]
Airfield Jet A-1	(i) Not recorded (ii) Relative humidity 46% Temp 23.5 - 23.4°C	(i) 43 ±4 (ii) 46 ±2
100% hydroprocessed jet fuel	Relative humidity 46% Temp 22.0 - 23.3°C	40 ±2
100% Merox jet fuel	Relative humidity 46% Temp 23.5 - 23.4°C	38 ±3
‘Conditioned’ (25°C, 100% relative humidity, stirred)		
Sample	Conditioning Period	Dissolved Water ppm [by mass]
Airfield Jet A-1	1 day	105 ±6
	5 days	108 ±13
	9 days	99 ±8
100% hydroprocessed jet fuel	2.5 days	97 ±6
	3.5 days	94 ±4
100% Merox jet fuel	1 day	104 ±3
	2.5 days	100 ±3

3.3 Effect of Static Dissipator Additive on Dissolved Water Uptake

Static dissipator additive (SDA) is known to increase the settling time⁹ of added free water droplets in the MSEP test for jet fuel. Limited tests were carried out to establish whether SDA might influence water uptake in two of the model hydrocarbons; Stadis 450 was used for this purpose. Samples of both toluene and n-octane were doped with 5ppm SDA, ‘conditioned’ as described previously and then tested for water content using the Karl Fischer coulometer. There was no significant difference in the water content between the toluene and n-octane samples with and without SDA, although the difference in conductivity between the doped and undoped samples was considerable.

3.4 Effect of Fuel Composition on Retention of Added Emulsified Water

Previous sections have discussed the uptake of dissolved water. It is also important to consider the retention of free, suspended water within the fuel. For this test, water was emulsified in the fuel or hydrocarbon by mixing 25ml water with 25ml fuel or hydrocarbon sample in a syringe using a 30 second high shear mixing cycle on an EMCEE Microseparometer. The mixture was left to settle in the syringe with a plunger in place to prevent water loss or ingress. After 24 hours the water content of the fuel layer, sampled from its mid-point, was determined by the Karl Fischer method.

Table 3 shows that there is no significant difference in the free water retention characteristics of the three fuels although the uncertainty in the measurement is larger due to the transient

nature of a settling emulsion.

Table 3 Effect of fuel/hydrocarbon composition on retention of added emulsified water

Sample	Total Water Content ppm [by mass]		
	'As-Received'	'Conditioned'	Sampled from fuel or hydrocarbon layer from the settled emulsion
N-octane	20 ±2	80 ±2	55 ±6
Methylcyclohexane	29 ±2	74 ±2	53 ±5
Toluene	78 ±3	566 ±10	484 ±8
Airfield fuel	46 ±2	102 ±8	85 ±5
Hydroprocessed fuel	40 ±2	96 ±5	80 ±12
Mercox fuel	38 ±3	102 ±4	112 ±20

3.5 Discussion of Water Characterisation Results

The tests have shown that it is possible to achieve controlled, reproducible concentrations of dissolved water in a fuel or hydrocarbon by stirring or agitating the sample and by controlling the temperature and relative humidity of its storage environment.

The saturated aromatic hydrocarbon was able to absorb seven times more dissolved water (and an even higher proportion of emulsified water) than the alkane or cycloalkane with a similar number of carbon atoms. The Jet A-1 fuels showed similar affinities for dissolved water, in both the 'as-received' and 'conditioned' states and all retained similar amounts of emulsified water. As noted in the UK Annual Survey of Aviation Fuel 2007¹⁰, typically the aromatics content of jet fuel is in the range 12% to 24%, with a mean aromatics concentration of 18.7% by volume. The Jet A-1 fuel specification has a maximum permitted aromatics content of 25% by volume. Data in Table 1 suggests that the water uptake of a fuel with 12% aromatics is likely to be less than fuel with 24% aromatics.

From the work on model solvents, a different ranking of dissolved water uptake by the fuels might have been predicted and a greater difference in the dissolved water content of the fuels would have been expected. This suggests that other constituents or additives in the fuels are somehow masking the water-absorbing properties of the aromatic components.

There is a complex interplay between dissolved and free water and the tests threw up an unusual result in that the water content was greater in 'conditioned' samples than in samples emulsified with excess water. This illustrates the real-world complexity of controlling the water content of fuels. The effect of SDA was not entirely clear. It is present in aviation fuels and is known to affect the water separation characteristics of the fuel. SDA could potentially mask any differences in free water shedding rate due to the chemical composition of the fuels but initial tests suggested that it had not influenced the concentration of water dissolved in the model hydrocarbons.

4. Study of Freezing/Melting Phenomena Using Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a thermoanalytical technique which measures the energy required to increase or decrease the temperature of a sample relative to a reference over a given temperature range. Phase transitions such as freezing and melting in the sample will involve enthalpy changes and these can be detected by DSC. Detecting the phase changes of water at concentrations of parts per million is challenging and approaching the limits of sensitivity of the DSC technique.

A Mettler Toledo DSC 1 was used for this work and the samples were sealed within standard 40 μ l aluminium crucibles. Samples were studied for a range of heating and cooling rates between 1°C/min and 20°C/min over the temperature range +50°C to -125°C. Reliable data was obtained between +20°C and -70°C; data outside this range was disregarded since the instrument was not under stable thermal control. The optimum cooling/heating rate regime was considered to be 10°C/minute. Rates higher than 10°C/minute gave improved resolution of the exotherms and endotherms attributed to water freezing and melting, but could introduce a thermal lag in the DSC curves. Slower rates gave very poor resolution of the exotherms and endotherms due to peak broadening.

In all cases, a fuel or hydrocarbon sample was cooled and then heated to observe enthalpy changes due to water freezing and melting; DSC scans were run in duplicate for all fuels and model hydrocarbons. Model hydrocarbons were tested in the 'conditioned' state only; fuels were tested for each of the following states:

- (i) 'as-received'
- (ii) 'conditioned'; the 'conditioned' samples were immediately sealed in the DSC sample crucibles after removal from the conditioning environment
- (iii) containing emulsified water, as described in section 3.4.

4.1 DSC Results – Cooling and Heating

A typical cooling thermogram is illustrated by Figure 1; similar curves were obtained for all the model hydrocarbons and fuels. Table 4 summarises results from the thermograms in terms of the freezing range and the peak freezing temperature.

Figure 1 DSC thermogram of airfield Jet A-1 cooled from 20°C to -70°C

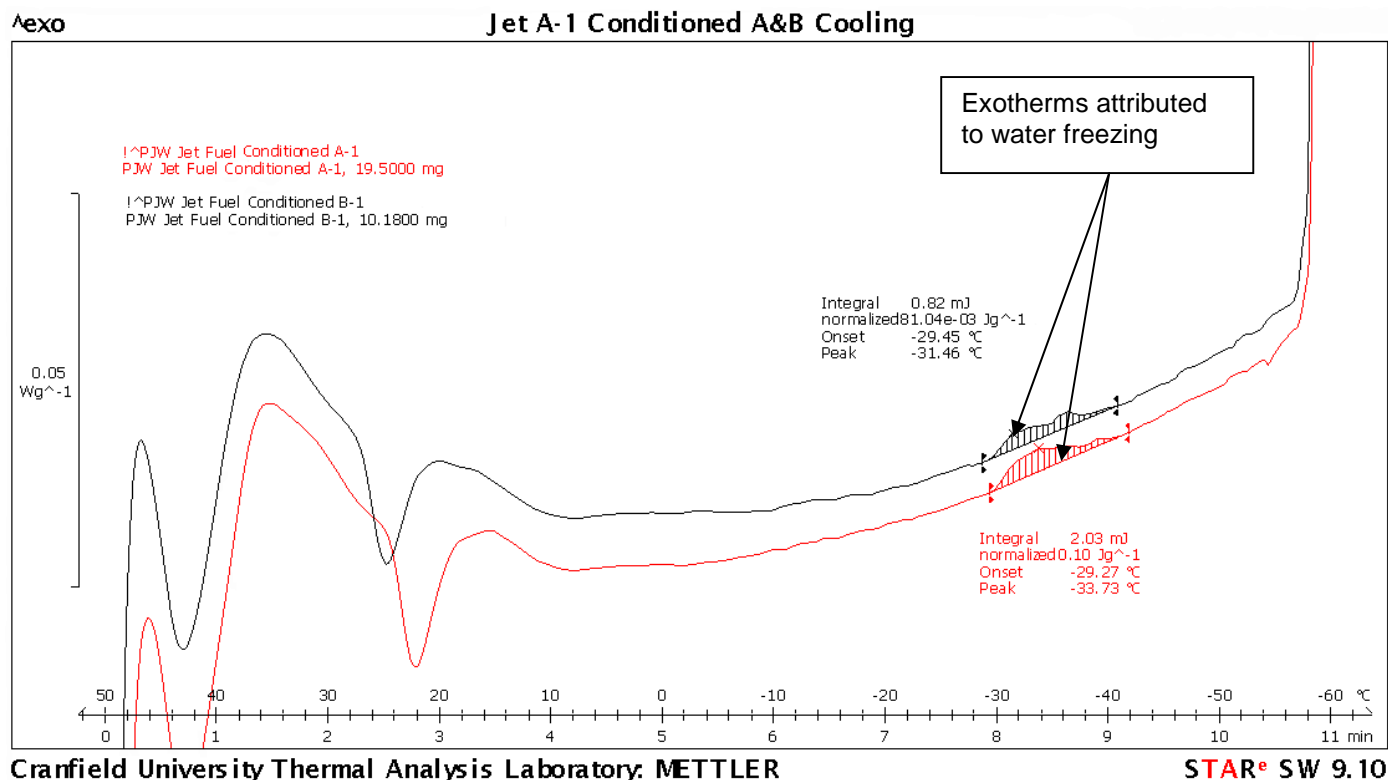


Table 4 DSC data on temperature range of water freezing in model hydrocarbons and fuels. Cooling rate 10°C/minute

Sample	Exotherm Range °C		Peak Temperature °C	
	Test 1	Test 2	Test 1	Test 2
N-octane, conditioned	-29 to -38	-27 to -40	-33	-33
Methylcyclohexane, conditioned	-30 to -40	-30 to -40	-33	-34
Toluene, conditioned	-32 to -44	-31 to -45	-38	-33
Airfield fuel, as-received	-30 to -39	-26 to -39	-33	-33
Airfield fuel, conditioned	-29 to -40	-29 to -41	-34	-31
Airfield fuel, emulsified	-28 to -41	-30 to -40	-33	-35
Hydroprocessed fuel, as-received	-30 to -38	-30 to -36	-33	-33
Hydroprocessed fuel, conditioned	-30 to -40	-30 to -40	-33	-32
Hydroprocessed fuel, emulsified	-30 to -37	-30 to -37	-33	-33
Mercox fuel, as-received	-27 to -38	-30 to -38	-32	-32
Mercox fuel, conditioned	-28 to -38	-30 to -38	-32	-32
Mercox fuel, emulsified	-30 to -38	-30 to -38	-33	-34

The DSC results suggest that for the model hydrocarbons, the dissolved water precipitated out of solution and solidified at temperatures in the range -27°C to -45°C with the typical peak freezing temperature being -33°C . For the fuels, both 'as-received' and 'conditioned', the dissolved water precipitated out of solution and froze at temperatures in the range -26°C to -41°C with the typical peak freezing temperature being -32°C or -33°C . Fuel containing emulsified water showed a similar range of water freezing temperature and peak freezing temperature behaviour.

Data from the heating thermograms is presented in Table 5 and a typical curve is depicted by Figure 2. Duplicate test data has been condensed into a single column; note that several curves showed two endotherms between 5 and 15°C apart. In all cases, the enthalpy of melting was very small, about one tenth of the enthalpy of freezing and around the detection limit of the method.

Figure 2 DSC thermogram of airfield Jet A-1 heated from -70°C to 20°C

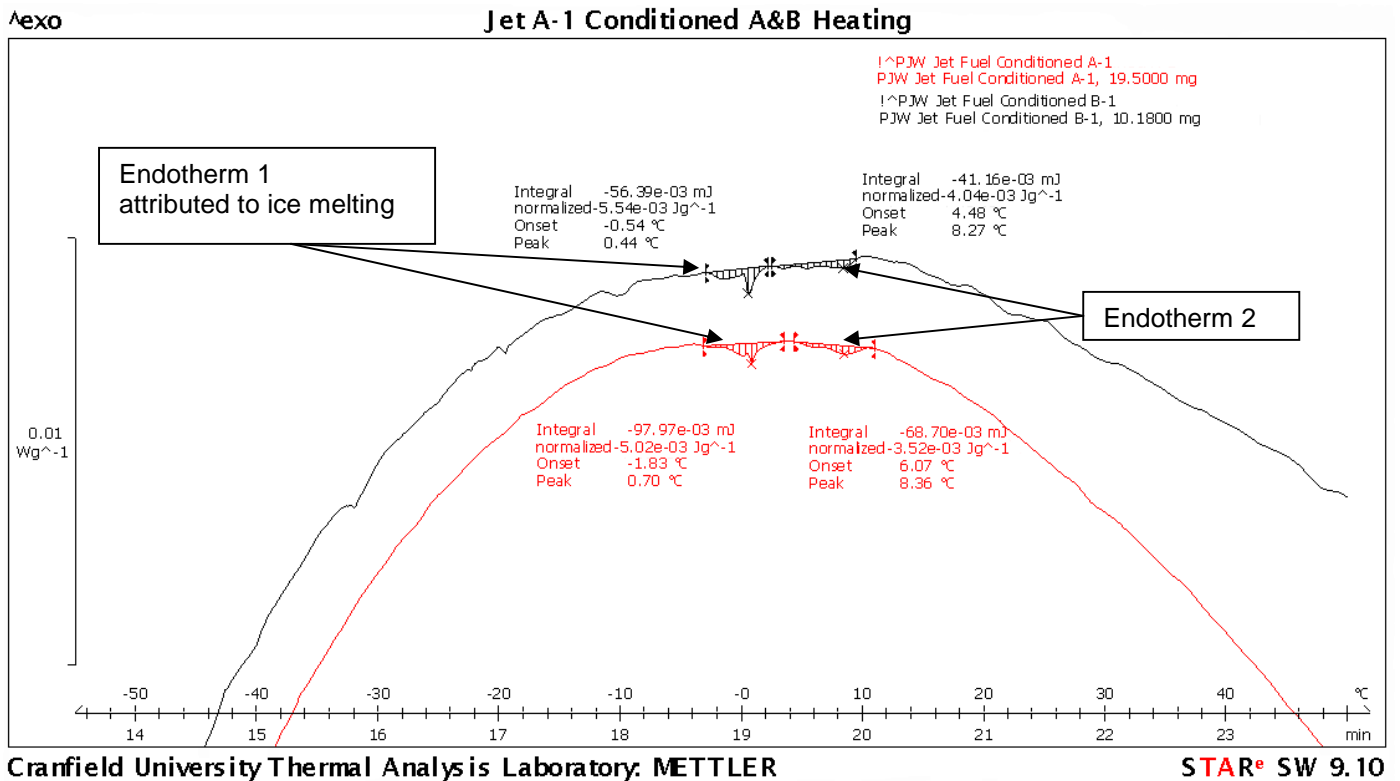


Table 5 DSC data on temperature range of water melting in model hydrocarbons and fuels.
Heating rate 10°C/minute

Sample	Endotherm 1		Endotherm 2	
	Range °C	Peak °C	Range °C	Peak °C
N-octane, conditioned	v small	v small	none	none
Methylcyclohexane, conditioned	-1 to +2	+0.6, +0.8	v small	v small
Toluene, conditioned	-20 to 0	-4, -0.2	none	none
Airfield fuel, as-received	-5 to +1	-1, -1	none	none
Airfield fuel, conditioned	-2 to +2	-0.7, +0.4	+4 to +10	+8, +10
Airfield fuel, emulsified	-5 to -0	-4, -3	+8 to +18	+15, +15
Hydroprocessed fuel, as-received	-2 to -2	0, 0.5	+4 to +11	+8, +8
Hydroprocessed fuel, conditioned	-0.4 to +2	+0.6, +0.6	none	none
Hydroprocessed fuel, emulsified	-0.6 to +2	+0.5, +0.6	v small	v small
Merox fuel, as-received	-2 to +2	+0.5, -0.8	+3 to +10	+5, +6
Merox fuel, conditioned	-0.4 to +2	+0.6, +0.6	v small	v small
Merox fuel, emulsified	-0.8 to +2	+0.6, +0.5	+4 to +10	+10, +8

4.2 Discussion of DSC Results

As has been noted, using DSC to detect phase changes in water at concentrations of parts per million is pushing the technique to the limits of its sensitivity; other small changes within the fuel or hydrocarbon sample could mask any real effects being measured. However, the exotherm on cooling the samples was identifiable and typically occurred in the range -26°C to -41°C, with a peak freezing temperature between -32°C and -34°C. This would be consistent with the water precipitating out of solution as minute droplets, as the fuel is cooled, but remaining as a supercooled liquid until it was able to nucleate homogeneously. Homogeneous nucleation would be the preferred crystal nucleation mode for very small water droplets with few impurities. These findings agree with reported¹¹ experimental studies of small water droplets (up to 50µm) homogeneously nucleating and freezing in cloud chambers in the temperature range -36°C to -40°C.

Tests on fuel samples containing emulsified water showed similar freezing characteristics to the 'as-received' and 'conditioned' samples. The water droplets still in suspension after several hours are probably 10µm or less in diameter and therefore unlikely to settle out; these might be expected to freeze in a similar way to small water droplets that have come out of solution.

The DSC endotherms attributed to ice melting were much less well defined. The reason for this is uncertain but a similar phenomenon has been observed in a study on jet fuel freezing¹². It could be an indication that frozen water droplets are being slowly reabsorbed in the fuel as the temperature increases or that the droplets froze as a water-fuel mixture, which has no sharply defined melting point. DSC studies suggest that, in all three fuels, the frozen water droplets were melting over a temperature range of -5°C to +2°C, with the typical peak melting temperature being +0.6°C. Similar results were noted for the model n-alkane and cycloalkane. Toluene, the model aromatic hydrocarbon, showed droplet melting from -20°C to 0°C.

The second endotherm, which occurred at several degrees Celsius above the melting point of ice, and was visible in some of the heating thermograms, is even harder to explain, but may be associated with system energy changes related to the solution of water in the fuel or melting of trace amounts of high molecular weight hydrocarbons in the fuels.

5. Study of Ice Crystal Formation in Fuels and Model Hydrocarbons

A Leica DM LM optical microscope fitted with a phase contrast system and Linkam THMS600 cold stage was selected as being suitable for investigating ice crystal formation in cooled fuels and hydrocarbons. The cold stage includes a micro heating element and automated liquid nitrogen cooling system to give accurate thermal control over a wide range of temperatures.

5.1 Sample Preparation and Selection

Sample preparation and cleanliness of the sample holder are important for optical microscopy, especially where nucleation of crystals at low temperature is to be studied.

For all the results presented in this report, the sample was contained in a small quartz crucible of approximately 400 μ l volume fitted with a cover slip. A rigorous cleaning regime was adopted for the crucible and cover. On each occasion, prior to use, crucible parts were cleaned with Decon 90 detergent, in an ultrasonic bath, rinsed twice in distilled water and dried with a hot air blower. The crucible was completely filled with the fuel or hydrocarbon being studied so that there were no air bubbles visible when the cover slip was applied. The crucible was placed in a carrier within the cold stage to allow visual scanning of the sample without opening the cold stage compartment.

To prevent condensation from forming on the windows of the cold stage, the interior was purged with dry nitrogen prior to cooling and, in operation, a steady stream of nitrogen was blown across the exterior surfaces.

Each of the fuels and model hydrocarbons described previously was studied in the microscope cold stage for a range of cooling regimes. As with any optical microscopy technique, at any one time only a small proportion of the sample is within the focal plane. For comparison of results the samples were studied near the midpoint of the sample depth and also at the bottom of the cell.

5.2 Cooling/Heating Regimes

The maximum freezing temperature specified for Jet A-1 is -47°C and the fuel temperature during flight should always be 3°C above the recorded fuel freezing temperature. For this reason, -44°C was chosen as the lower temperature limit for many of the fuel microscopy studies.

The fast cooling rate was chosen as 10°C per minute as this was the rate used in the DSC thermography tests; a slow cooling rate of 1°C per minute was selected to establish whether precipitation of water and nucleation of ice was a time dependent process. A third cooling

regime was based on real aircraft data. The fuel temperature during the last flight of G-YMMM from Beijing to London Heathrow was recorded prior to a hard landing at Heathrow Airport in January 2008; a simplified version of the fuel temperature profile given in the AAIB final report¹³ was adopted to find out if anomalous icing occurred under such conditions. The lowest recorded fuel temperature in the aircraft was -34°C ; this was reduced to -47°C for the laboratory tests.

Table 6 Heating and cooling regimes used in the microscopy studies

Thermal regime	Details
Fast heat/cool cycle	Cool at $10^{\circ}\text{C}/\text{min}$ from 25°C to -44°C Hold at -44°C for 30 min Heat at $10^{\circ}\text{C}/\text{min}$ from -44°C to 25°C
Slow heat/cool cycle	Cool at $1^{\circ}\text{C}/\text{min}$ from 25°C to -44°C Hold at -44°C for 30 min Heat at $1^{\circ}\text{C}/\text{min}$ from -44°C to 25°C
AAIB report ¹³ cooling regime	Cool at $1^{\circ}\text{C}/\text{min}$ from 25°C to -2°C Hold at -2°C for 40 min Cool at $0.15^{\circ}\text{C}/\text{min}$ from -2°C to -20°C Cool at $0.05^{\circ}\text{C}/\text{min}$ from -20°C to -47°C Hold at -47°C for 80 min Heat at $2^{\circ}\text{C}/\text{min}$ from -47°C to 25°C

5.3 Microscopy Results – Model Hydrocarbons

‘Conditioned’ samples of all three model hydrocarbons were cooled to -44°C using the fast and slow heating/cooling cycles shown in Table 6. Microscopy observations are summarised in Table 7.

Water droplets were observed to precipitate out of the hydrocarbons as the temperature decreased. Droplet size was measured at intervals and droplets were observed, using phase contrast, for changes in shape or optical appearance which might indicate the formation of ice crystals. Images were captured at pre-programmed intervals.

For the fast cooling rate tests, significant turbulence was observed within the samples; convection currents could be seen with water/ice particles swirling around within the crucible. The water/ice particles observed were $5\mu\text{m}$ or less in size. As the temperature decreased, some of the white water droplets adopted a pink/blue hue. It was not clear whether the water droplets had indeed frozen, but in a spherical form, or were still in a supercooled state. On heating, the droplets began to disappear and all re-dissolved by 25°C .

For the slow cooling rate tests, there were no visible convection currents; water/ice particles of 2 to $3\mu\text{m}$ developed at the bottom of the crucible and not within the body of the sample for n-octane and methylcyclohexane. As noted for the fast cooling rate tests, it was not clear whether the water droplets actually froze. As the samples were heated from -44°C to 25°C , the droplets began to re-dissolve and by 25°C they had all disappeared back into solution.

Toluene behaved differently to the alkane and cyclic hydrocarbon under slow cooling conditions. On cooling, identifiable ice crystals formed on the bottom of the crucible. The exact temperature of the appearance of the first ice crystals still has to be determined, but water droplets and crystals were in co-existence at -35°C . On cooling further to -44°C , the ice crystals grew and the surrounding water droplets decreased in number. On reheating the toluene, the water droplets began to disappear, leaving the ice crystals intact; the ice crystals finally melted at around 0°C .

Plate 1 Toluene on slow cooling to -35°C , showing ice crystals and 2 to $12\mu\text{m}$ droplets on the bottom of the crucible. Note that toluene was the only sample tested that showed ice crystal structures.

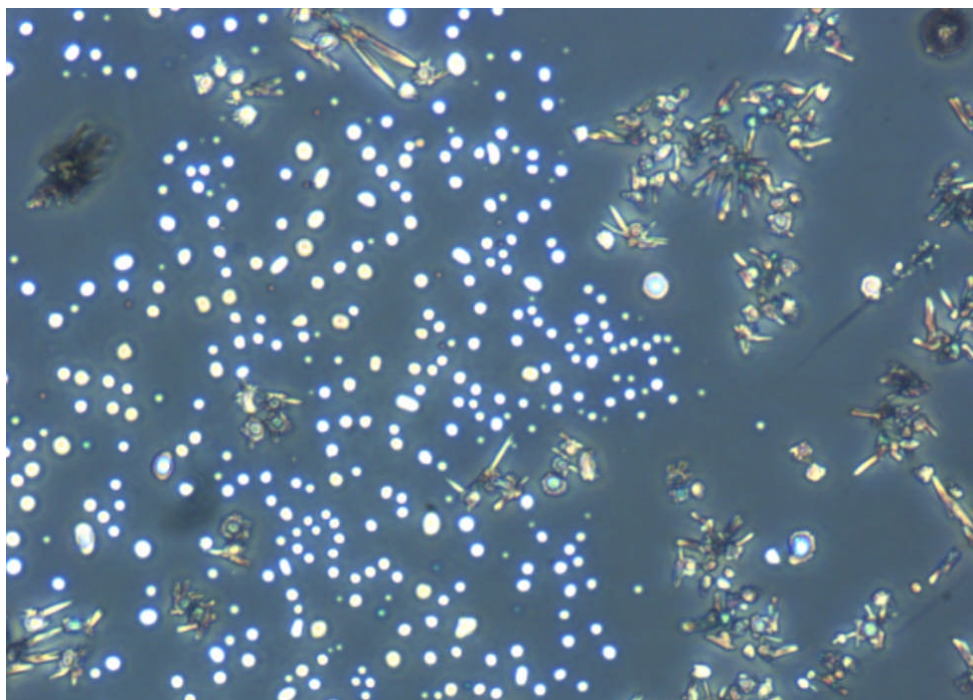


Plate 2 Toluene on slow cooling to -44°C , showing ice crystals and 2 to $12\mu\text{m}$ droplets on the bottom of the crucible. Note that compared with Plate 1, the ice crystals have grown at the expense of the droplets.

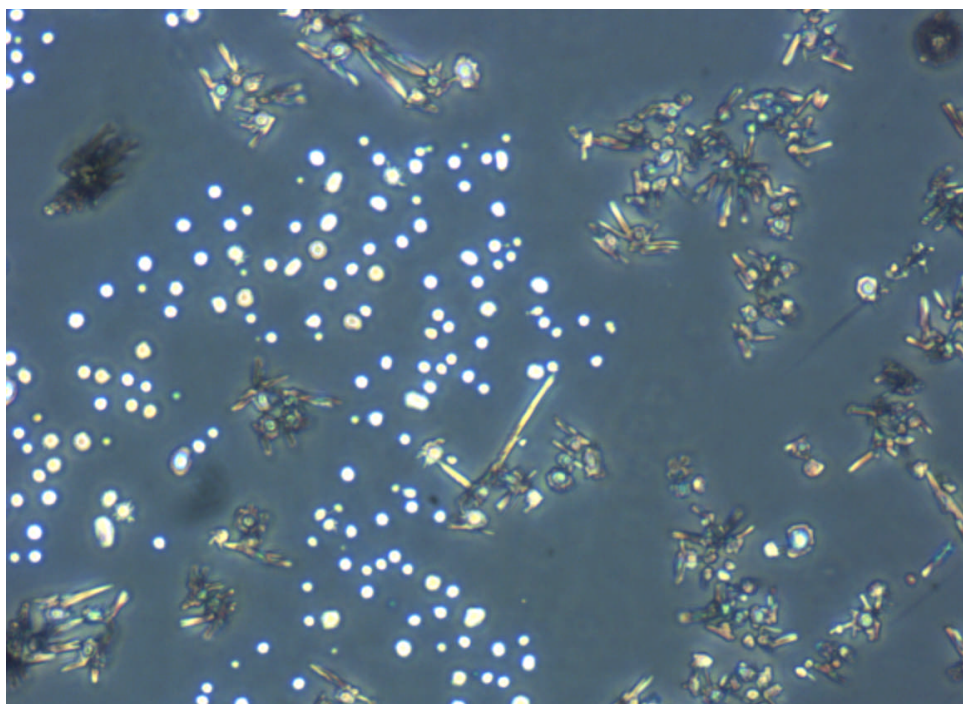


Table 7 Water/ice particle sizes for model hydrocarbons experiencing slow and fast cooling regimes

'Conditioned' Sample	Water/Ice Particle Size μm		Appearance of Ice Crystals
	Slow cool	Fast cool	
N-octane	2 to 3 crucible bottom mainly	4 to 5 crucible middle mainly	None observed. Blue/white droplets
Methylcyclohexane	3 crucible bottom mainly	2 to 3 crucible middle mainly	None observed. Blue/white droplets
Toluene	2 to 12 crucible bottom mainly	2 to 3 crucible middle mainly	Crystals noted. White droplets

5.4 Microscopy Results – Fuels

'Conditioned' samples of all three jet fuels were cooled to -44°C using the cooling regimes given in Table 6.

For all three fuels, the size of the water droplets observed was 5µm or less as noted in Table 8; the cooling rate appeared to have little effect on the droplet size. Optical microscopy could not quantify differences in the number of water particles with changes in temperature or cooling rate.

There was no hard evidence of the water droplets changing to crystalline ice formations. However, as the temperature was lowered some of the white water droplets adopted a pink/blue colour. On holding the temperature at -44°C, a few clusters of water droplets were observed. On heating, the droplets began to disappear and all had vanished by 25°C.

Table 8 Water/ice particle sizes for fuels experiencing different cooling regimes

'Conditioned' Sample	Water/Ice Particle Size µm			Appearance of Particles
	Slow cool	Fast cool	AAIB regime	
Airfield fuel	1 to 2	2 to 5	2 to 5	White water droplets, changing to pink/blue drops at lower temperatures. Appearance of a few strings and clusters of droplets at low temperatures
Hydroprocessed fuel	2 to 3	2 to 3	-	
Mercox fuel	1 to 3	≤ 2	-	

5.5 Discussion of Microscopy Results

Visual observations confirmed that for all the samples tested, dissolved water came out of solution in the form of small droplets of size 5µm and below, as the fuel or hydrocarbon was cooled; droplets disappeared back into solution when it was heated. The size of the water droplets did not appear to be affected by the rate of cooling or the composition of the fuel/hydrocarbon.

There was no visual evidence of ice crystal formation in any of the three fuels when cooled to -44°C under either fast or slow cooling regimes. Some droplets adopted a pink/blue hue at lower temperatures, but it was uncertain if this was due to freezing (as spherical droplets), supercooling of the water in the droplets or just an optical effect. Some strings of water droplets were observed suggesting that the droplets had clustered and/or frozen together. The alkane and cycloalkane model solvents showed the same low temperature behaviour as the three fuels. Toluene, the aromatic model solvent, behaved very differently to the fuels and other hydrocarbons at low temperatures; ice crystals and water droplets formed at low temperatures. As the toluene was reheated from -44°C, the water droplets began to disappear above -15°C and the ice crystals melted at around 0°C. An explanation for the formation of ice crystals in toluene is that toluene has an ability to dissolve a much higher concentration of dissolved water at 25°C compared with the other hydrocarbons, as shown in Table 2.3. The interaction and interchange of water between the dissolved state, supercooled water droplets and ice crystals is complex and requires further investigation.

Until recently, it was assumed that water freezing in fuel adopted the hexagonal ice crystalline structure, I_h , the only form considered to be stable under the conditions experienced by fuel in an aircraft. This assumption was recently challenged in work by Murray et al¹⁴ where it was suggested that supercooled water droplets below 10µm can crystallise to ice in the cubic I_c form.

Ice Ic is metastable and can convert readily to ice Ih; ice Ih has never been found to convert to ice Ic.

Murray et al studied the formation of ice in supercooled water droplets suspended in an oil matrix. By surrounding the droplets in an oil matrix, mass transfer via the vapour phase was blocked which simplified the study of the solid-state transformation from Ic to Ih. Their results showed that, typically, water droplets of diameter $5\mu\text{m}$ and below froze predominantly to cubic ice. As the size of the water droplet increased from $5\mu\text{m}$ to $17\mu\text{m}$, the formation of the stable phase of ice Ih was favoured. This suggests that the water droplets of $5\mu\text{m}$ and below formed in the fuels and model hydrocarbons could freeze to the metastable ice form and then undergo a phase transition to ice Ih as the temperature increases.

The final proportion of Ic in a particular frozen droplet is dependent on the relative rates of heat dissipation and heat production in an individual droplet during the freezing process¹⁵. If the droplet heats up sufficiently, the ice Ic of the initial crystal nucleus and the initial crystalline form, will subsequently be transformed to ice Ih. Heat transfer therefore appears to play a significant role in this process; it can explain the relationship between droplet size and the presence of ice Ic, and also the effect thermal conductivity of the environment surrounding the droplet has on the formation of ice Ic.

Vapour pressure has also been predicted to play a role in the transformation of Ic to Ih. The vapour pressure of Ic has been measured to be approximately 11% higher than that of Ih at temperatures of -93 to -83°C . This means that where the two crystalline forms exist in close proximity, the water will diffuse from the Ic to the Ih crystal and the Ih crystals will grow at the expense of the Ic crystals, which consequently decrease in size. This could explain the observation in toluene that the ice crystals grew and the surrounding droplets decreased in number as shown by comparison of Plates 1 and 2.

6. Conclusions

Studies of water uptake in model hydrocarbons suggest that the aromatic component of the fuel will have the most influence on the uptake and release of water; the studies showed that an aromatic hydrocarbon could contain up to seven times more dissolved water than an n-alkane or cycloalkane with a similar number of carbon atoms. However, there is not a clear-cut relationship between aromatics content and the affinity for water of a fuel, and the effects of aromatics are likely to be masked by natural surfactants in the fuel. The role of fuel composition is further complicated by the presence of static dissipator additive which is known to affect water shedding in fuels.

Tests to examine the behaviour of water in aviation fuel, showed that water which was dissolved in jet fuel precipitated out of solution in the form of small droplets of size $5\mu\text{m}$ and below as the fuel was cooled. These droplets disappeared back into solution in the fuel when it was re-heated. The initial studies indicate that the droplet size is not affected by cooling rate. The droplets remained as spherical particles when cooled to the freezing temperature of the fuel and there was no indication of ice crystals being nucleated. From visual observations it was assumed that the droplets either contained supercooled water or water frozen as spheres.

However, DSC studies indicated that the water actually froze between -26°C and -41°C . Ice crystals were formed in toluene (the model aromatic hydrocarbon) on cooling to -44°C but identifiable ice crystals were not observed in the other fuels or hydrocarbons. The reason for ice crystal formation in toluene is believed to be associated with its higher affinity for water. Further investigation is required, especially as the crystalline form of the ice formed from small droplets is uncertain.

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