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The future for heating in the UK: Surfactant stabilised formulations for improving energy transfer

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The future for heating in the UK: Surfactant stabilised formulations for improving energy transfer

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Abstract
Next to transport, the heating and cooling[1] of our buildings is the largest user of energy in the UK. Around 35% of UK energy is used in this way and 80% to 85%[2] of this energy is used to heat water in our heating systems. While the design of the hardware of heating systems has been optimised, nobody has paid much attention to the water heated by boilers and circulated through radiators and fan coils to warm our houses and buildings. Water is an inexpensive, safe material which conducts heat. It is not very efficient as an energy transporter however, because to put it simply, water is not wet.

There is now a group of silicone-based surfactants that can, at low concentration, reduce the surface tension of water to about 20 mN/m, and the contact angle between water and a solid (steel in a radiator) to 0°. A zero-contact angle means complete wettability. This type of surfactant is known as a super spreader. It has been demonstrated that complete wettability caused by a zero-degree contact angle means that 3 times as much water is present on a surface than can be achieved by using a standard Alkyl Poly Glycoside (APG) based surfactant.

Applying this technology to a building heating system means that a small amount of this superspreader, dosed into the water in a heating system will ensure that spaces heat faster, and boilers operate less, saving an estimated 20% of the energy previously used. The superspreader has been commercialised and this product will give a payback of less than one year – based on current energy costs. If this technology were applied to the water of every water based heating and chilled water system in the UK the yearly energy saving would equate to the annual output of 2 Drax B[3] power stations.

End Use	Domestic	Services	Industry	Transport	Total	Total excluding transport
Space Heating	28,728	10,084	3109	-	41,922	41,922
Water Heating	7,494	1,953	-		9,477	9,477
Process Use	-	-	9,082		9,082	9,082
Cooking /Catering	1,108	2,042			3,150	3,150
Drying /Separation			1,762		1,762	1,762
Heat Total	37,330	14,079	13,954		66,363	66,363
Non Heat Uses	6,464	6,006	5,535	53,418	71,423	18,005
Total	43,794	20,085	19,489	53,418	136,786	83,368
Percentage Used for heating 85 %		70 %	72 %		48%	78 %

Table 1: How energy is used in the United Kingdom, (UK government figures 2013)[4]

Introduction
Almost 40% of all the energy used in the UK is used to heat our homes and places of work. Nearly all this energy (85%) is used to heat water. This water is heated in boilers, by heat pumps or other means to temperatures up to 80°C and circulated through radiators or fan coils to heat individual spaces. The efficiency of boilers, heat pumps etc and radiator/fan coil design has been optimised to the extent that further improvements would not improve fuel savings.

Until recently, nobody has paid much attention to the water that flows in the closed heating loop, believing that water is the ideal cheap, safe, and thermally stable heat transfer medium. Its efficiency for transferring heat from the boiler to the air in a room has been taken for granted. Water, however, is a poor conducting medium, because it is not very wet and makes poor contact with the metal surface of a radiator or fan coil.

While Wilson postulated that the surface tension of water is related to its thermal conductance 10 years ago, it is only in the past 2-3 years that others have published papers indicating agreement. The surface tension of water is related to the angle which a drop of water makes with a surface. This is known as the contact angle. The addition of a low concentration of a surfactant will significantly reduce the surface tension of water and also reduce the contact angle, increasing the water contact with the surface, and make water wetter. This is important because the metal surface of a radiator is full of tiny micro and nano crevices that water cannot enter. This is the basis of commercial products already on the market.

At The University of the West of Scotland, Dr Yaseen's research lab has shown that water containing a superspreader surfactant will heat a room much faster than water itself and faster than water containing other surfactants. More importantly water containing a superspreader surfactant with nanomaterial formulation will heat a room faster than water containing metal or graphene nanoparticles on its own. Nanoparticles make the water more thermally conductive, with surfactants being important because they make the surface wetter.

Product development history
In 2008[5], it was noted that a surfactant solution introduced to clean 6 heating systems in Council properties in Cumbernauld caused building occupants to open windows in December to stay cool. The radiators were noticeably hotter and further investigation indicated that this improved heating had been achieved using less gas than would be expected. The phenomenon was short lived however as the surfactant used was not thermally stable, it quickly degraded, and its benefit lost.

Surfactants and their effect on energy improvement in a water environment were already being investigated. Professor Gad Hestroni looked at thermally stable Alkyl Polyglucosides to improve saltwater evaporation and demonstrated that less energy was used to evaporate water in a vat when the surfactant was added. He attributed the improvement in the pool boiling situation to the way water boiled in contact with a hot surface[6]. Water containing surfactant boils producing a myriad of minute bubbles which transmit energy much faster into the bulk fluid. Untreated water produces loose large bubbles that are less efficient energy transmitters. Hestroni's work showed that Alkyl Polyglucoside was a thermally stable surfactant that could improve energy efficiency under boiling conditions. It did not explain why radiators should become hotter in a central heating system however, as only a very small proportion of the circulating water in a heating circuit contacts hot metal in the boiler.

Faced with this issue Wilson proposed that the improvement in radiator temperature must be associated with the reduced surface tension of the water in the circuit caused by the presence of the surfactant. He suggested that the lower surface tension allowed water to access more of the radiator surface improving heat transfer through the radiator. Treatments based on APG (mainly coco glucoside) have been commercialised and these have delivered around 10%-15% energy savings. The main reason proposed for their working is that they lower surface tension and allow the water to access more of the radiator or fan coil surface.[7]

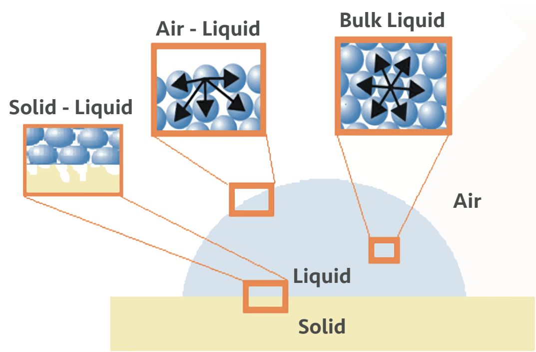
This report investigates the mode of action of surfactants further and updates the thinking on how surfactants and polymers work before indicating how further improvements are possible.

The role of fluid properties
Metal surfaces are not smooth and contain micro-indentations or microcracks. Nano crevices are also being investigated.[8] Water which has high surface tension, ca 70 mN/m at 70°C to 80°C, will sit on top of most of these micro/nano indentations thus having a lower surface contact. Agents that reduce the surface tension of water can result in better wetting and improved surface contact at the metal – liquid interface. The addition of 1000 ppm of certain surfactants to water reduces its surface tension down to ca 30 mN/m, improving the wettability of water and enhancing "liquid – metal" contact and therefore improving the transfer of heat. This mechanism has only recently been acknowledged in a peer reviewed journal[9] stating that fluid physical properties play a large part in energy transfer and emphasising surface tension as being an important factor.

The Role of Surfactants
Surfactants have already been used in the UK, North America and in many other countries as energy saving products and this capability has been heavily linked to the ability of these surface-active agents to lower the surface tension of water and therefore decrease the contact angle water makes with the surface allowing more of the surface to be wetted. However, while surfactants like alkyl polyglucosides reduce surface tension of water they still do not allow water to access the complete surface, as the contact angle with a metal surface is still around 40°. Wettability depends on the interfacial tension between water and the metal surface. This is the adhesive force between the water and the metal, and the higher this force is, the wetter the surface will be.

This increased wettability has resulted in commercial surfactant-based products reducing energy use in many building heating and chilled water systems by between 10% and 15%. While these surfactants reduce the surface tension of water, this still does not ensure that all the radiator surface is accessed by the water.

Surface wettability and contact angle
Surfactants are used as wetting agents and their addition spreads the water and changes the angle at which water contacts the substrate (metal in the case of a heating or chilled water system). This angle is referred to as the contact angle. The lower the contact angle the more the surface is wetted. When the contact angle between the water and pipe surface is zero then the whole surface is wetted. This is the ideal as water is contacting every part of the surface. It is not easy to achieve a contact angle of zero between water and a surface. It requires a very special surfactant or a special modification of the surface.



1. The high surface tension of water at the solid-liquid interface means that water cannot enter the microcracks on the metal surface.

2. The high surface tension of water at the air-liquid interface means that a paperclip can float on water, or a mayfly can walk across its surface.

Fig. 1 shows the force in bulk of water, with that at the air-liquid interface at which water molecule bonding cannot interact with air thus there is greater bonding at surface molecule resulting in surface tension force. At solid-liquid the metal interface is rough at the micro-nano scale resulting in reduced contact. Surfactants can reduce potential interfacial surface tension both at solid-liquid and at air-liquid or water interface also.

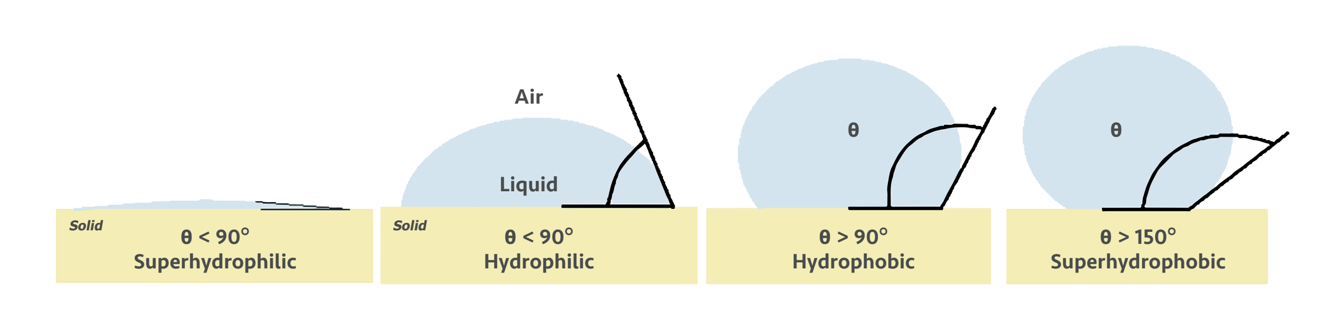


Fig. 2. A schematic showing surface contact angle (θ) for Superhydrophobic Hydrophobic & also Hydrophilic material. A balance between adhesive and cohesive forces influences degree of wetting or wettability.

Contact angle and surface coverage
While the optimum wettability in terms of surface coverage is zero, it is difficult to know what that means in terms of quantity of water on a surface. This was established for polyvinylidene difluoride PVDF[10] by Joanna Kujawa et al. In this work the surface of Polyvinyl di fluoride (PVDF) was modified by using nanoparticles to give surfaces where the contact angle of water on the surface could be changed down to a contact angle of 6° with water.

The relationship between surface coverage and contact angle is shown in the figure 3 below. This relationship shows that a contact angle of 6° means that approximately 2.5 times as much water contacts the surface as when the contact angle is 45°, the contact angle achieved by most APG type surfactants.

This suggests that a surfactant that could achieve a very low contact angle on a radiator surface would give a much better surface coverage and transfer of energy than one which gave a contact angle of 45°. Yuting et al[11] demonstrated that the surfactant molecules adsorbed onto the solid surface play a prominent role in enhancing interfacial heat conduction. The analysis of density and temperature distributions revealed the dynamic transfer process of thermal energy at the interfaces where the thermal energy in the solid wall is transferred mainly to the surfactant molecules, and the surfactant molecules further transfer the energy to the solvent molecules. This process increases the total heat transfer across the solid liquid interface, as shown in Fig. 4 on the next page.

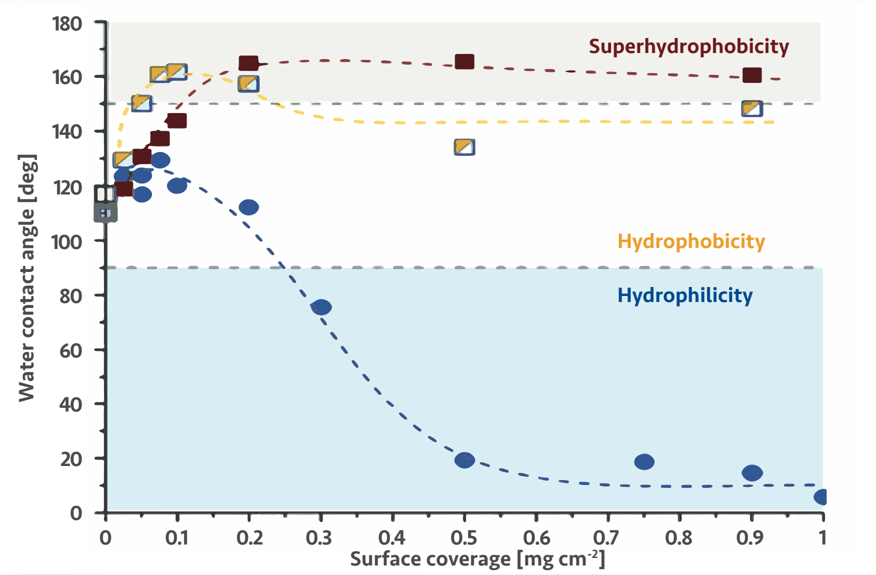


Fig. 3. Shows relationship between contact angle and surface coverage. *From C Joanna Kujawa et al Carbon nanohorn improved durable PVDF membranes - The future of membrane distillation and desalination Joanna Kujawa et al. Desalination 511 (2021) 115 117.*

It was therefore considered that the ideal surfactant to improve thermal conductance was a product that when mixed with water, would produce a very low contact angle. The product should also have excellent surface adsorption properties. This profile aligned with non-ionic silicone surfactants or silicone polyethers. We have, therefore found a material that has excellent wetting credentials, produces a contact angle on surfaces close to zero, and works on almost all surfaces. This product, that has good water miscibility, is thermally stable and is biodegradable[12].

This non-ionic silicone-based surfactant contains both a water-insoluble silicone backbone and several water-soluble polyether pendant groups that can result in increased wettability. This type of surfactant not only greatly reduces the surface tension of water, producing a 0° contact angle, but increases the adhesive forces that bind water to the surface material. The product is 70% biodegradable. (See reference 12).

Proof of concept
The University of the West of Scotland found a novel way of demonstrating that this molecule, could deliver better thermal conductance than other products. They constructed a heavily insulated box to simulate a room[13] and placed a heating coil inside. The liquid which filled the coil was heated to a constant temperature of 66°C and circulated continuously through the coil. The temperature that the air space reached within the box was measured against the heating time and recorded by two thermal probes. The results were recorded by a data logger as obtained from the Thermal box shown in Figure 5 on the next page.

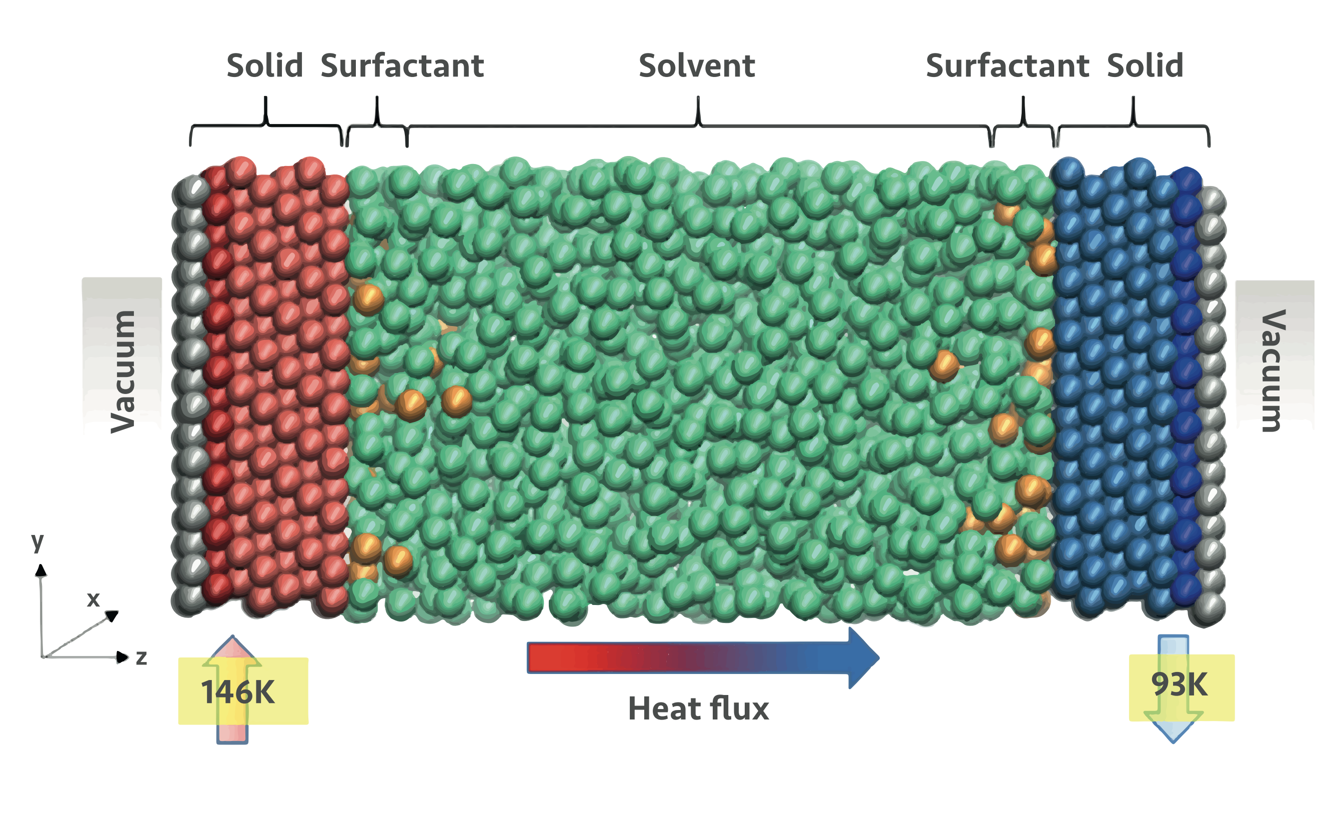


Fig. 4. Heat flow model; The diagram of the heat flow model, where the positions of the outermost layers of the solid (silver colour) are fixed, the dark red layer is set as the heat source, the red layers are the solid on the high temperature side, the blue layers are the solid on the low temperature side, the dark blue layer is set as the heat sink, the orange spheres are the surfactant molecules, and the green spheres are the solvent molecules
From Yuting G.et al. *A molecular dynamics study on the effect of surfactant adsorption on heat transfer at solid-liquid interface. International Journal of Heat and Mass Transfer 135(2019) 115- 123.*

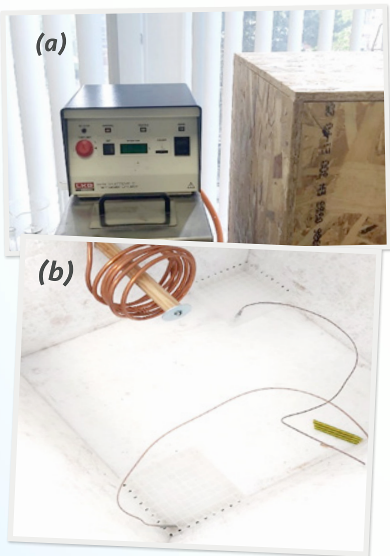


Fig. 5. (a) Thermal box with controller, (b) Photograph of inside of box with heating coil.

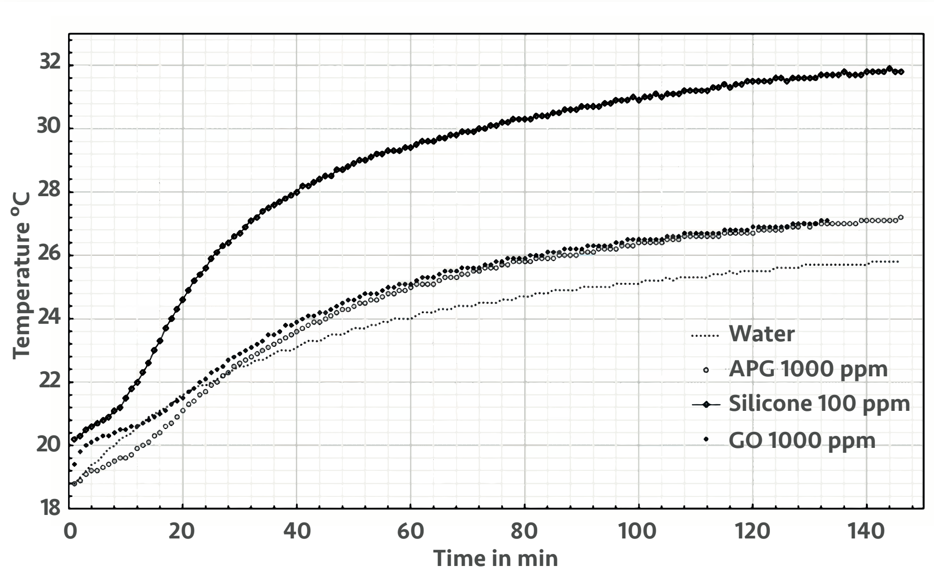


Fig. 6. Thermal Box Comparison of Silicone product with water and water +APG

Note. The contact angle of water is 80°, the contact angle of water containing 1000 ppm alkyl poly glucoside is 40° and the contact angle of water containing Delta T is 0°. This graph shows that the lower the contact angle, the wetter the surface and the better the transfer of heat from the radiator.

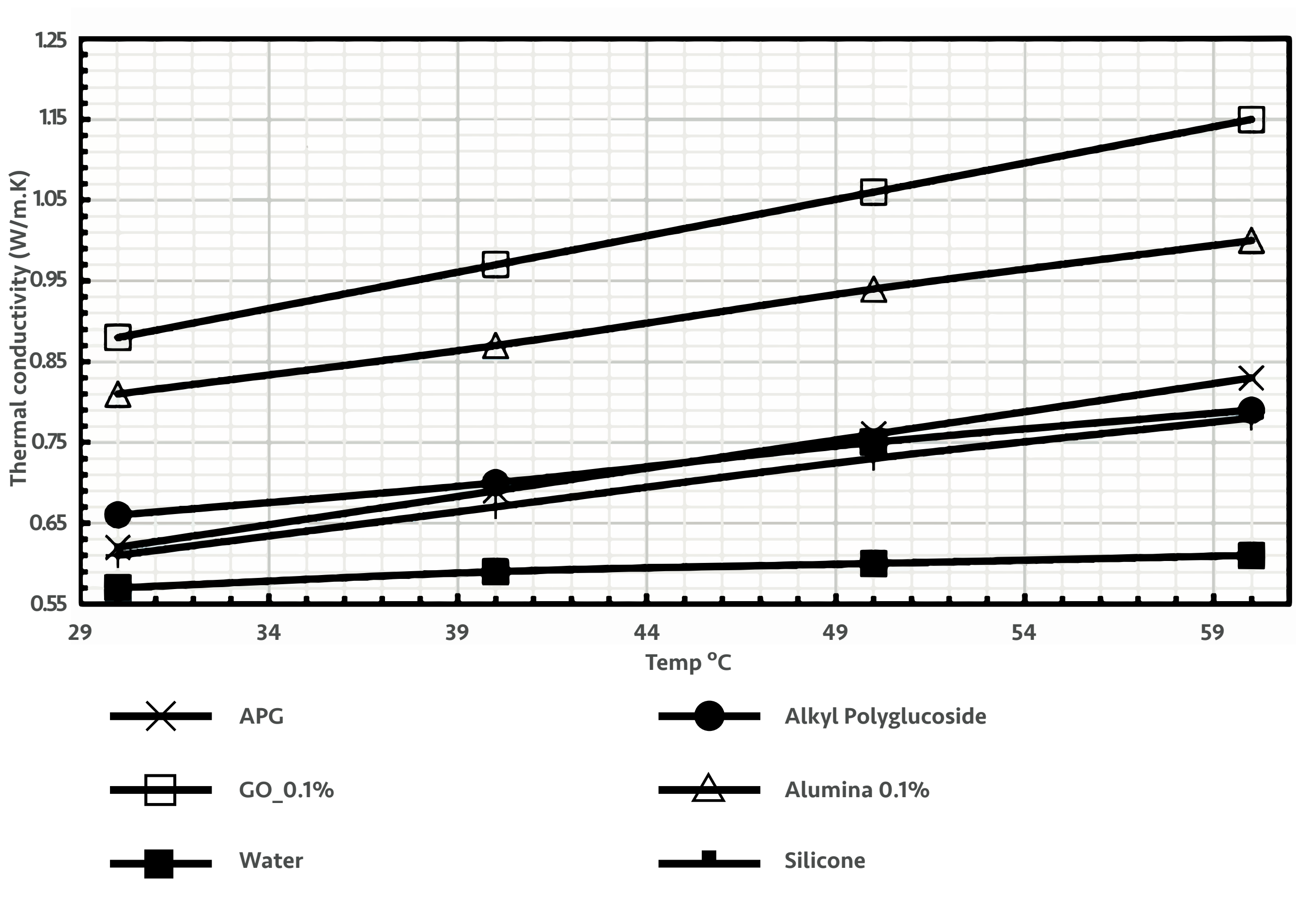


Fig. 7. Thermal conductivity of additives to water

This graph compares the thermal conductance shown when various types of nanoparticles are added to water. Optimum thermal conductance is achieved using graphene oxide nanoparticles, **but this still does not** match the performance of the silicone product.

The Silicone surfactant does not significantly change the thermal conductance of water. Neither do the other surfactants tested. Graphene oxide and aluminium nanoparticles have a greater effect on thermal conductance. Neither of them performs as well alone as the silicone product in the Thermal Box Test.

Conclusions

The addition of a surfactant to water lowers the surface tension of water and also changes the contact angle at a water / solid interface. Lowering of the contact angle results in an increase of surface wetting or water to surface contact potential. This improved surface contact means that any thermal energy contained in the water will be transferred to the metal more effectively. It is thought that the surfactant acting at the surface also plays a role in this thermal transfer through pool boiling.

Complete surface contact by water is achieved when the contact angle at the water / solid interface is zero or close to zero, and this can be achieved by a group of chemicals known as super spreaders.

Complete wetting of the surface means that water and the energy it contains gets on to the entire surface of a radiator or fan coil unit heating or cooling a space much more quickly allowing the thermostat to shut down the boiler or compressor more quickly. This has the potential to save around 20% of the energy currently used within such a system.

In terms of energy transfer, super spreaders are superior to nanoparticle treatments that operate by increasing the thermal conductance of water.

This study demonstrates that by producing a zero-degree contact angle on a metal surface maximises the energy transfer between boiler output and heat transferred into a room. We believe that conservatively this product will reduce the energy requirements of water based heating and chilled water systems by 20%. Applied throughout the UK this would save the energy output of 2 x a Drax B power station.

This product has been commercialised by SafeSol Ltd. under the brand name Delta T. The product has a pending patent application number 2313080.0.

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References

1 This paper will focus on heating systems as these are the most used in the UK. In other parts of the world, like the Middle East, Chilled water systems designed to keep buildings cool would be more prevalent.

2 *https://www.statista.com/statistics/426988/united-kingdom-uk-heating-methods/*

3 Drax B produces 6% of the country's energy needs. It has a capacity of 3,906 MW based on coal and biomass.

4 *www.gov.uk/government/collections/energy-consumption-in-the-uk*

5 This phenomenon was not recorded but following it, the author decided to investigate other work being carried out on surfactants. Much of it, at the time, focussed on Pool Boiling or flows in microchannels.

6 Hetsroni G. Gurevich M.et al The Effect of Surfactants on Boiling Heat Transfer . DOI;10.1615/ICHMT. 2004.Int. ThermSciSemin80.

7 International Patent Additives for Wet Heating and Cooling Systems 18th August 2016 (WO2016/128724A1).

8 Wang Y. and Keblinski P. Role of wetting and nanoscale roughness on thermal conductance at liquid-solid interface Appl. Phys. Lett. 99, 073112 (2011); *https://doi.org/10.1063/1.3626850*.

9 E Vaishnavi K. et al The effect of surface tension on the thermal performance of a pulsating heat pipe – a review international Journal of Research in Engineering IT and Social Sciences ISSN 2250-0588 Volume 10 Issue 06 June2020 pps 29-34.

10 C Joanna Kujawa et al Carbon nanohorn improved durable PVDF membranes - The future of membrane distillation and desalination Joanna Kujawa et al. Desalination 511 (2021) 115 117.

11 Yuting G.et al. A molecular dynamics study on the effect of surfactant adsorption on heat transfer at solid-liquid interface. International Journal of Heat and Mass Transfer 135(2019) 115- 123.

12 The Silicone surfactant is approximately 70% by weight polyethylene oxide. In this sustainable product, the polyethylene oxide is derived from sugar cane. The remaining portion of the molecule is silicone which is primarily derived from minerals.

13 The outside ambient temperature is measured before each new test so slight adjustments can be made, if required, to eliminate influence of external temperature effects.

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