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Crystallisation of sodium dodecyl sulfate and the corresponding effect of 1-dodecanol addition**Emily Summerton¹, Georgina Zimbitas¹, Melanie Britton², Serafim Bakalis¹**¹**School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham, B15 2TT**²**School of Chemistry, University of Birmingham, Edgbaston, Birmingham, B15 2TT****Abstract**

Sodium dodecyl sulfate (SDS) exhibits crystallisation upon exposure to low temperatures, which can pose a problem in terms of product stability. In this study, non-isothermal crystallisation of SDS is investigated via differential scanning calorimetry (DSC) at concentrations that are typical of those present in many industrial liquid detergents. At different low temperatures, the crystal structures are analysed with X-ray diffraction (XRD) and it is concluded that ice formation during the surfactant crystallisation process occurs below 0 °C. The capability of the alcohol precursor, 1-dodecanol, as a seeding material for SDS crystallisation is also investigated through the use of DSC and optical microscopy. These results show that 1-dodecanol can successfully act as a seed for SDS crystallisation. Upon cooling an SDS aqueous system, the crystallisation peak in the DSC thermogram shifts to a higher temperature in the presence of 1-dodecanol. Therefore, any remnant alcohol precursor in surfactant-based formulations could have a negative impact on the product stability upon exposure to cold climates.

Keywords: A1 Nucleation; A1 Differential scanning calorimetry; A1 Optical microscopy; A2 Industrial crystallisation; B1 1-dodecanol; B1 Sodium dodecyl sulfate

1. Introduction

The leading players in the fast moving consumer goods (FMCG) industry provide over 400 brands worldwide and involve products being sold on a short timescale at a relatively low cost. The FMCG industry can be further subcategorised into separate sectors including food and beverages, personal care, homecare and beauty care. New products are added to the portfolios on a regular basis in order to maintain market leadership. The 2017 forecasted revenue for the laundry care and detergent sector is US \$85 billion with a compound annual growth rate of 5.1 %, illustrating the sheer size of this particular industry [1]. Within this sector, each brand is

manufactured to specific consumer requirements in terms of supply volume and packaging material. Depending on the product formulation and nature of the local consumer market, the volume supplied can range from millilitres to litres. However, at all product scales it is an essential requirement that the formulation demonstrates stability during the stages of manufacture, transport and the subsequent shelf life [2], with a two year shelf life period commonly expected for the majority of homecare brands. This is particularly challenging for liquid products in regions where there is potential exposure to cold climates. Under such temperature conditions, there can be a risk of surfactant crystallisation, which, in turn, can affect product appearance. Within the detergent industry there are stability test methods in place to predict and minimise crystallisation failures [3]. Since the detergent and laundry care industry continues to expand globally, there a need to further broaden knowledge of surfactant crystallisation. This understanding will enable product stability and the accompanying test methods to be further optimised.

Typical liquid detergent formulations have a complex composition, with surfactants and water as the major components, alongside other additives such as perfumes, dyes and preservatives. The surfactants are essential in providing the necessary functions of detergent products through their cleaning and foaming properties. These formulations tend to contain a variety of different surfactants, with some of anionic nature and others of a non-ionic basis. It is this combination that provides the optimum characteristics. The major component is the anionic surfactants, which exhibit excellent soil removal properties and come at a relatively low cost. However, the minor presence of non-ionic surfactants is also important due to their foaming ability and low temperature stability properties. Sodium dodecyl sulfate (SDS) [4, 5] and N, N-dimethyl dodecyl amine oxide (DDAO) [6] are examples of widely used anionic and non-ionic surfactants, respectively.

Above the critical micelle concentration (CMC), surfactant and mixed surfactant systems can form micellar aggregates. This concentration can be determined by conductivity and surface tension measurements [7]. Aside from concentration, temperature also plays an important role in the process. The minimum temperature that is required for micelle formation is termed the Krafft temperature. Below this point, aggregates cannot form and there is a risk of surfactant crystallisation. The Krafft temperature of an aqueous ionic surfactant system can be lowered upon addition of a non-ionic surfactant [8, 9]. The non-ionic surfactant inserts into the aggregates and reduces the repulsion between the charged head groups, resulting in non-ideal micelles. Thus, the degree of micellization increases and the CMC is reduced. The solubility product of the surfactant salt no longer equals the product of surfactant monomer concentration and counter ion concentration. As a result, a lower temperature

is required for precipitation to occur. Aside from the addition of non-ionic surfactants, the structural features of the surfactant can also influence its Krafft temperature. In 1991, Gu et al. investigated the structural variability relationship with Krafft temperature, providing an empirical formulae for the Krafft temperature dependency [10].

The crystallisation of surfactants consists of two processes; nucleation and crystal growth [11]. Nucleation can be defined as the start of the phase transition where surfactant molecules aggregate into clusters constituting the nuclei. [11] Crystals will only grow from nuclei above a critical radius. The rate of nucleation is the limiting factor at the beginning of the crystallisation process. As the amount of nuclei increase, the rate of the phase transition also increases and then subsequently slows towards the end of the phase transition as the newly crystallised phase provides a boundary for the further growth. A S-shaped rate profile is typical for such systems [12].

In the literature, there are relatively few reports regarding the crystallisation of SDS solutions, despite the importance of sulfated surfactants in the detergent industry. In 2001, Smith et al. reported the crystallisation transitions for a SDS solutions over a range of concentrations up to a maximum of 20 wt. % SDS. This investigation employed various techniques, including differential scanning calorimetry (DSC) and turbidity measurements [13, 14]. Their work also considered the morphology of the SDS crystals. This was further investigated by Chantraine et al. using X-ray diffraction (XRD), Raman spectroscopy and scanning electron microscopy (SEM) [15, 16]. Crystallisation studies of other single surfactant systems are limited in the literature; Fu-Gen Wu et al. investigated the cooling crystallisation of the cationic surfactant CTAB to provide further knowledge regarding the various metaphases [17]. The mechanism and accompanying kinetics of the crystallisation were examined via the use of optical microscopy and DSC. The work of De Anda et al. on the crystallisation of glutamic acid emphasises the importance of image analysis when determining a mechanism and associated morphological changes in the structural conformation [18]. In addition to single surfactant systems, crystallisation of anionic and non-ionic surfactant mixtures is also a field with few publications [5, 9, 19].

Aside from additional surfactants, other components can affect the crystallisation of an ionic surfactant. For example, the presence of short and long chain alcohols can influence crystallisation behaviour. SDS is manufactured from its alcohol precursor, 1-dodecanol, through sulfation under a selected set of conditions [20]. During the manufacturing process, incomplete conversion results in some 1-dodecanol remaining in the

solution. Investigations into SDS and 1-dodecanol mixtures are limited with one example being a study into the development of a model distinguishing between the presence of SDS and 1-dodecanol via surface tension isotherms [21]. Earlier studies have focused on the structural effects that short chain alcohols and phenols have on SDS complexes. These investigations used small angle neutron scattering (SANS), XRD and pulsed field nuclear magnetic resonance (NMR) [22, 23]. In a separate study, the thermodynamic properties of SDS solutions mixed with various short chain alcohols were used to support the hypothesis of a hydrogen bonding interaction between the two components [24]. Longer chain alcohol addition to SDS solutions results in a lowering of the Krafft temperature upon dissolution of small quantities of hexanol, heptanol and octanol [25]. However, an investigation into Krafft temperature variation for an SDS solution upon addition of 1-dodecanol does not seem to appear in the literature, despite it being the alcohol precursor.

In this paper, SDS crystallisation will be discussed for a range of aqueous concentrations that are commonly present in the dish liquid supplied by industrial manufacturers. An understanding of surfactant crystallisation is vital when controlling and improving the low temperature stability test methods for detergent products. The understanding of SDS-alcohol aqueous systems is the focus for the second part of the study where the effect of 1-dodecanol addition on SDS crystallisation will be reported.

2. Materials and Methods

Experimental work involved initial preparation of the surfactant solutions followed by exposure to cooling and heating cycles to enable crystallisation and subsequent melting to occur. These processes were monitored through a variety of techniques, which are described below.

2.1 Materials

SDS was purchased from Fischer Scientific (> 97.5 %). Aqueous solutions of SDS in the concentration range 10 - 30 wt. % were used throughout the study with 20 wt. % as the main system of interest. All solutions were freshly prepared with distilled water so as to minimise deviations due to hydrolysis.

1-dodecanol was purchased from Sigma Aldrich (> 98 %). Its melting point is approximately 24 °C so it exhibits extremely low aqueous solubility at room temperature. 1-dodecanol was present in a 5 wt. % concentration in the surfactant solutions.

2.2 Differential scanning calorimetry

Thermograms of the SDS solutions were obtained through use of a micro DSC (Sentaram model) with distilled water as the reference sample. For each sample run, approximately 70 mg of the sample and reference were measured into their respective cells and placed into the DSC furnace chamber. Each experiment was repeated a minimum of two times.

The lowest available cooling and subsequent heating scan rate of 0.1 °C/min was utilised throughout the non-isothermal DSC studies. The upper temperature was in the range of 30 - 40 °C with the lower limit being - 5 °C. A 20 minute holding time was applied at the maximum and minimum temperature points.

Having investigated the crystallisation kinetics of SDS aqueous systems, the addition of 1-dodecanol into the system was then studied via DSC. Due to its low solubility, 1-dodecanol was added directly into the DSC furnace cell. Shifts in crystallisation and melting temperatures were recorded, with the results being discussed in terms of the characteristics of the alcohol surfactant system. The scan rate used for these experiments was also 0.1 °C/min.

2.3 Optical microscopy

An optical microscope, model Leica Z16 APOA, was coupled with a Linkam LTS120 Peltier stage and used to observe the crystallisation phase transition of a 3 g sample of 20 wt.% SDS solution with and without 1-dodecanol addition. A 1 °C/min cooling rate was used. Limitations in the microscope and Peltier stage equipment meant that it was not possible to venture below this cooling rate with this method. Despite the differences in experimental cooling rates between DSC and optical microscopy measurements, comparisons could still be made between the two techniques as to the overall effect of 1-dodecanol addition.

2.4 X-ray diffraction

A powder diffractometer, model Siemens D5000, was used in combination with a cyropad to obtain diffraction patterns for 20 wt. % SDS solutions upon crystallisation at various low temperatures, namely 0 °C and - 20 °C. 1.5 mm borosilicate glass capillaries were filled with the respective solution to a level of approximately 4 cm. The capillary was then attached to the base and aligned before being inserted into the diffractometer. Subsequently, the capillary solution was cooled consecutively to the selected temperatures. At each temperature, a hold time of 15 minutes was programmed prior to measurement.

3. Results and Discussion

Characteristics of SDS and SDS-1-dodecanol systems at low temperatures were investigated. Particular areas of interest include crystallisation temperature variability with concentration and the nature of the precipitate.

3.1 Effect of concentration on crystallisation temperature

Figures 1a and 1b display typical DSC thermograms for a 20 wt. % SDS solution when exposed to a cooling and a subsequent heating cycle. Upon cooling one exothermic peak is observed for all concentrations, with the peak maxima relating to the crystallisation temperature and the area to the enthalpy in J/g. With regards to the heating cycle, a broad peak is typically observed at all concentrations.

Figure 2 displays the variation in crystallisation temperature with SDS aqueous concentration. Up to 20 wt. % - 23 wt. %, a linear correlation between SDS concentration and crystallisation temperature is attained. Beyond this concentration range, the variability in crystallisation temperature is minimal. The temperature that crystallisation can occur in such a system can be affected by both kinetic and thermodynamic effects. Melting transitions are largely driven by an entropic thermodynamic effect whereas nucleation and crystal growth are more likely dependent on kinetic effects. The rate of the crystallisation, and hence the temperature of phase transition, is governed by the nucleation and subsequent crystal growth [11]. During nucleation surrounding surfactant molecules collide and form clusters. If these clusters exceed a critical radius, they can then grow into crystals. When the SDS concentration is below 20 - 23 wt. % the limitation factor is likely the collision frequency. As the concentration is increased the collision frequency increases, and hence the nucleation time is reduced. However, beyond a 20 - 23 wt. % concentration the crystallisation temperature remains approximately constant. The Krafft point for an SDS solution is reported as approximately 15 °C [26]. Beyond this temperature, the solution can form micellar aggregates eliminating any possibility for crystallisation.

Figures 3a and 3b display plots for the enthalpy in J/g of solution and in J/g of SDS for the various aqueous systems. As deduced from Figure 3a, the enthalpy of the overall system increases with concentration of surfactant. This is attributed to the amount of SDS per gram of solution. This is further evident from the plot in Figure 3b where the enthalpy remains approximately constant.

3.2. Composition of precipitate

The crystallisation of a 20 wt. % SDS solution was further investigated by XRD, which enables one to infer information about the crystal structure. In Figure 4, the black line and red line correspond to XRD patterns obtained at the sample temperatures of 0 °C and - 20 °C respectively.

The powder diffraction patterns at the two respective temperatures overlap with each other, with the exception of three additional peaks in the - 20 °C pattern. These additional peaks are matched to ice and assigned the blue lines in Figure 4. Hence, it is possible to deduce that ice does not appear at 0 °C but it is present when the sample temperature is lowered to - 20 °C. DSC measurements are in agreement with this finding since no ice formation is evident when the temperature limit is - 5 °C. However, if the cooling cycle is taken to lower temperatures, the DSC thermogram displays a peak for water freezing at - 10 °C. Aside from the ice peaks the remaining peaks in the two XRD patterns match, indicating there is no structural change between the two SDS crystal structures.

3.4 Dodecanol Addition

Having discussed non-isothermal SDS crystallisation, the presence of its alcohol precursor on the kinetics will now be considered. Remnant alcohol precursors may be present in some detergent products as a result of incomplete conversion to their respective sulfated surfactants. Although the percentage of this impurity will be minimal, the 1-dodecanol used in this investigation is set at a 5 wt. % concentration as a result of practical laboratory limitations. Although at a higher concentration than found in industry, the behaviour in this system is expected to be indicative of the influence of 1-dodecanol.

It is possible to determine the change in crystallisation and subsequent melting temperatures upon addition of 1-dodecanol through the appearance of any peak shifting in the DSC thermogram. From the red line, in Figure 5 it can be deduced that SDS crystallises at 13 °C when no other excipients, except water, are present. The black line is for an aqueous solution of 1-dodecanol in the absence of SDS. A crystallisation temperature of 24.4 °C and a lower peak at 9.2 °C is observed for this solution [27]. The peak at 24.4 °C has a distinctly different shape to other peaks in the same region which can be attributed to the order of the phase transition. The peak at 24.4 °C can be related to the crystallisation of the alcohol alone [27], but the lower peak must relate to an alcohol-water phase, since these are the only two components present. Finally, the blue line is for a mixed SDS-dodecanol aqueous system. In the mixed system there are also peaks below 10 °C that may also correspond to the water-alcohol phase for in the 1-dodecanol aqueous system.

At the higher temperature end, the SDS-1-dodecanol system displays two overlapping peaks at 20.2°C and 23.5 °C. The hypothesis is that 1-dodecanol acts as a seed for the crystallisation of SDS. Seeds tend to be effective if they are of the correct size and have a similar chemical composition or structure to the sample to be crystallised in situ, as is the case of SDS with 1-dodecanol [28]. The existence of two peaks may likely be due to a SDS-alcohol polymorph and the subsequent higher peak can be attributed to excess 1-dodecanol. Repeated cycles eliminate the additional higher peak with the remaining overall peak shifting to the right. Upon repeat of the cycle the system has more time to pack into an optimum structure so as to incorporate the added 1-dodecanol in a co-crystal formation. Co-crystal formation is attributed to the similar structural properties between the two components.

Although the focus of this paper has been on the crystallisation phase transitions of SDS and SDS-1-dodecanol systems it is important to include the effect of 1-dodecanol on the melting transition, as acquired by DSC studies. Figure 6 displays the melting transition for a 5 wt. % aqueous solution of 1-dodecanol (black line), 20 wt. % SDS (red line) and a combined SDS-dodecanol aqueous system (blue line) as they are exposed to a heating cycle from - 5 °C at a consistent scan rate of 0.1 °C/min.

Aqueous 1-dodecanol exhibits two sharp melting peaks upon heating. From data previously reported [27], it is known that a pure 1-dodecanol system exhibits only one melting peak at 17.6 °C, as matched to one of the peaks in Figure 6. Appearing at approximately 25 °C, the other peak for the aqueous 1-dodecanol system is attributed to a 1-dodecanol-water phase since these are the only components present. The two peaks from the aqueous 1-dodecanol system demonstrate a sharp overlap with two from the mixed alcohol-SDS system. Hence, these peaks in the mixed system can be assigned to the same phases. The remaining peak in the SDS-1-dodecanol system has a maximum in excess of 30 °C. It can be concluded that the SDS aqueous system melts over a wider and lower temperature range when 1-dodecanol is not present. In addition to facilitating the crystallisation of SDS at a higher temperature, 1-dodecanol also stabilises the crystal, enabling it to remain in crystalline form to a higher temperature point.

3.5 1-dodecanol SDS crystallisation trigger mechanism

From DSC studies, it is inferred that the 1-dodecanol facilitates the crystallisation of SDS. It has been hypothesised that such a phenomenon is due to the low solubility of 1-dodecanol. Short chain alcohols have been reported to insert into, and stabilise, micelles [25]. However, 1-dodecanol is immiscible in SDS aqueous solution. Insoluble globules are only observed when 1-dodecanol is added to the surfactant solution, suggesting

the composition of these features is 1-dodecanol. These insoluble 1-dodecanol globules can act as seeds for crystallisation due to the similarity in the structure between 1-dodecanol and SDS. Through optical microscopy, it is possible to further determine the mechanism by which this occurs, as in the image sequence provided in Figure 7.

On cooling the mixed system, crystallisation of the globules themselves is initially observed with subsequent crystallisation of the surrounding SDS. These images clearly demonstrate the seeding capability of 1-dodecanol on SDS solution. Further experiments are also in agreement. The crystallisation appearing in the top left of the images is a result of crystallisation surrounding another globule. On further cooling, complete crystallisation of the system is observed at approximately 23 °C. When examining 20 wt. % SDS systems without the addition of 1-dodecanol and at the same cooling rate and system volume, crystallisation is not observed until 7 °C with complete crystallisation occurring at 0 °C.

4. Conclusions

The crystallisation of aqueous SDS systems upon cooling was observed via DSC and optical microscopy. Results indicate the crystallisation temperature is dependent on SDS concentration, specifically for concentrations below 20 wt. % where a linear increase in crystallisation temperature with concentration is observed. This linear relationship is likely to be due to an increased nucleation rate. At higher SDS concentrations, precipitation occurs immediately as the Krafft temperature is reached. XRD studies further support the existence of crystallisation of the SDS system and suggests ice is formed in this anionic surfactant system upon further cooling of the system below 0 °C.

Knowledge of the effect of 1-dodecanol on SDS crystallisation provides understanding for the potential of unsulfonated material for inducing crystallisation. Due to the seeding potential of 1-dodecanol, shifts in the phase transition temperature are observed during both the cooling and subsequent melting process.

Understanding the phase transitional behaviour in SDS has allowed for an increased understanding in one of the most widely used surfactants in the detergent industry. For the first time, the effect of its alcohol precursor is demonstrated to have a profound effect on the crystallisation and subsequent melting in such systems. This is of specific industry importance when there is a risk of some remnant alcohol precursor remaining in a surfactant system that could have a negative effect on stability.

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Fig 1 DSC cooling thermogram (a) and heating thermogram (b) for a 20 wt. % SDS solution attained at a scan rate of 0.1 °C/min

Fig 2 A plot showing the crystallisation temperature of the SDS aqueous solution versus the concentration of SDS

Fig 3 Plots of SDS solution concentration variability with enthalpy of crystallisation in J/g of surfactant solution (a) and in J/g of SDS (b)

Fig 4 XRD powder diffraction pattern for a 20 wt. % SDS solution taken at hold temperatures of 0 °C (black line) and - 20 °C (red line) with the blue lines highlighting those peaks that can be matched to those of ice

Fig 5 (a) DSC thermogram for SDS, 1-dodecanol and mixed SDS and 1-dodecanol aqueous systems; (b) is a larger image of the area of importance which is highlighted by the dashed line box in (a)

Fig 6 DSC thermograms for the melting transitions that occur upon for an aqueous solution of 20 wt. % SDS (black line), 1-dodecanol (red line) and the mixed alcohol-SDS system (blue line) on heating from -5 °C at a scan rate of 0.1 °C/min

Fig 7 Optical images for a 20 wt. % SDS and 5 wt. % 1-dodecanol aqueous solution upon cooling, taken at a selection of temperatures

Fig 1a

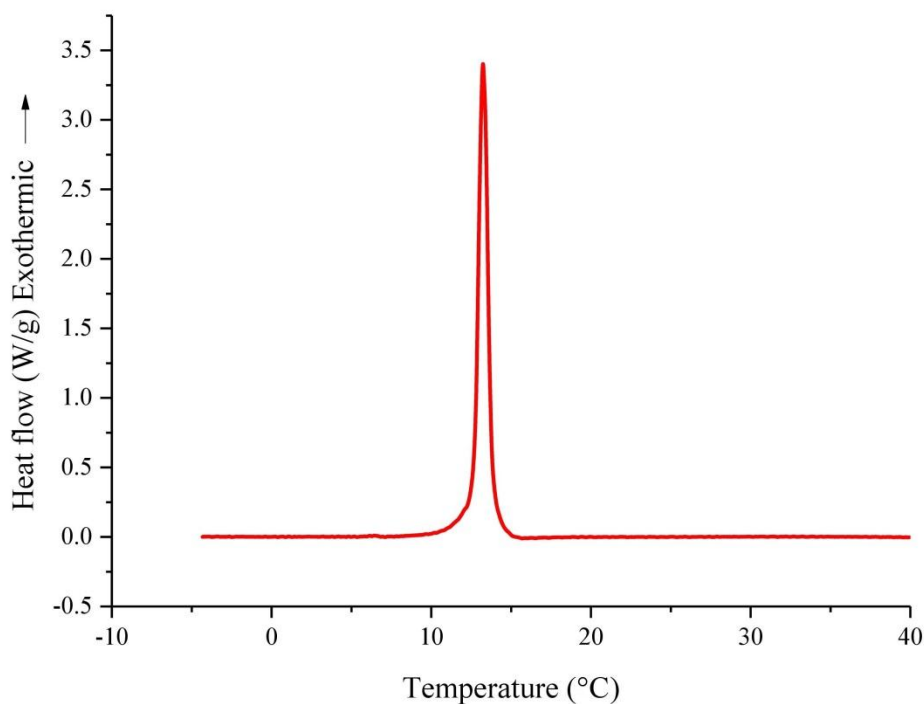


Fig 1b

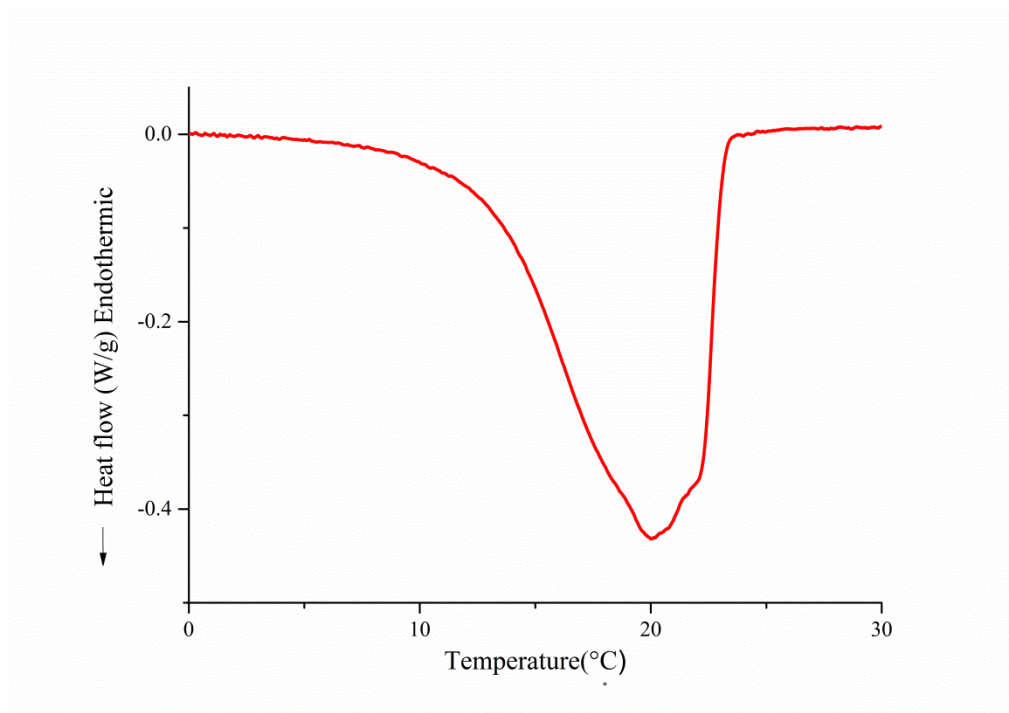


Fig 2

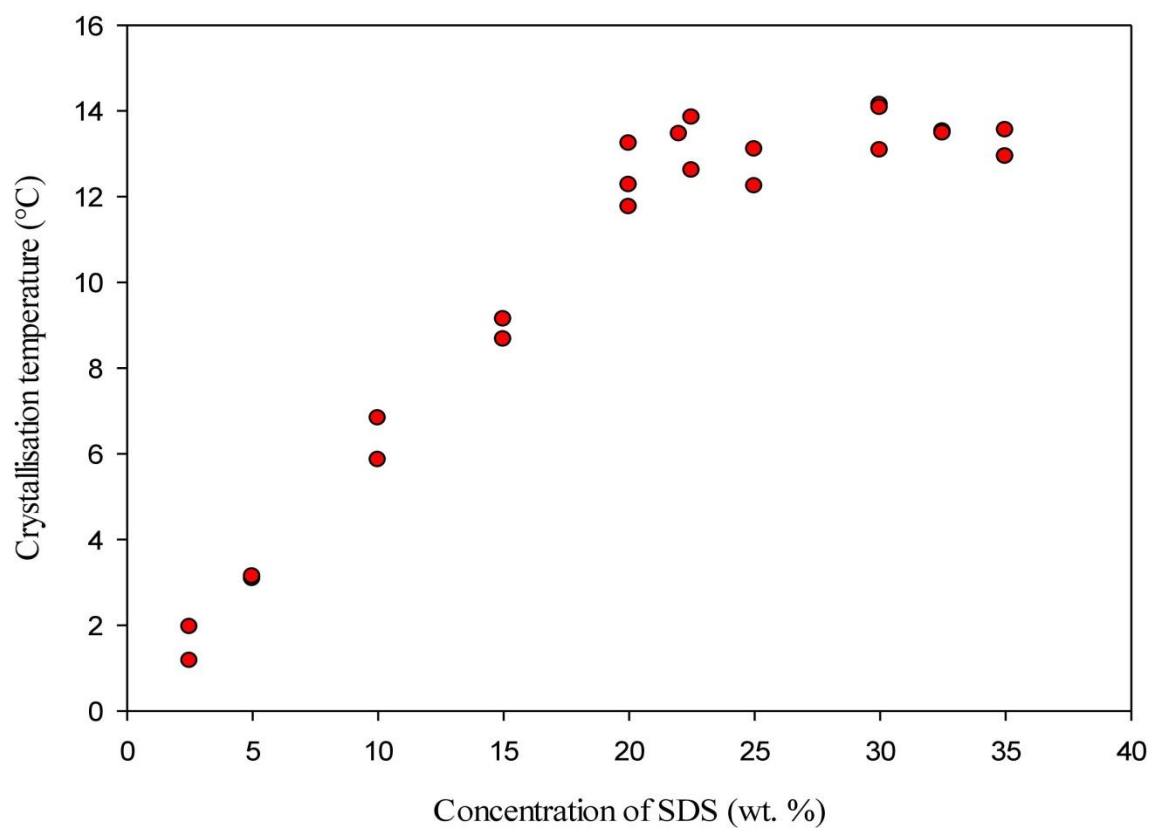


Fig 3a

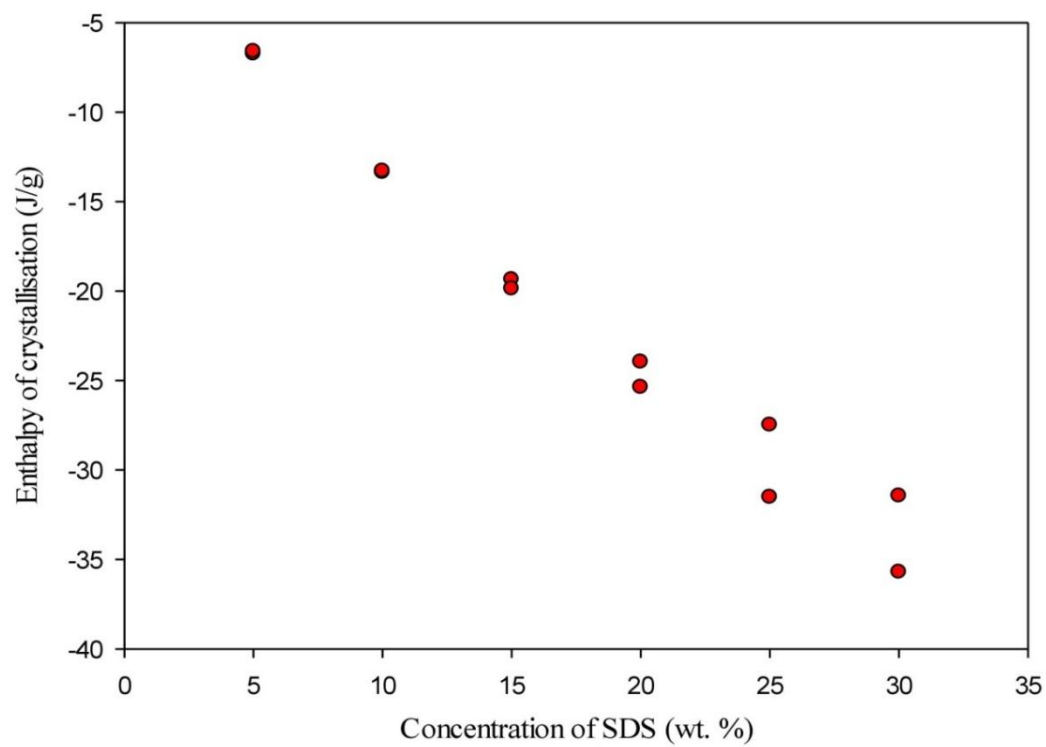


Fig 3b

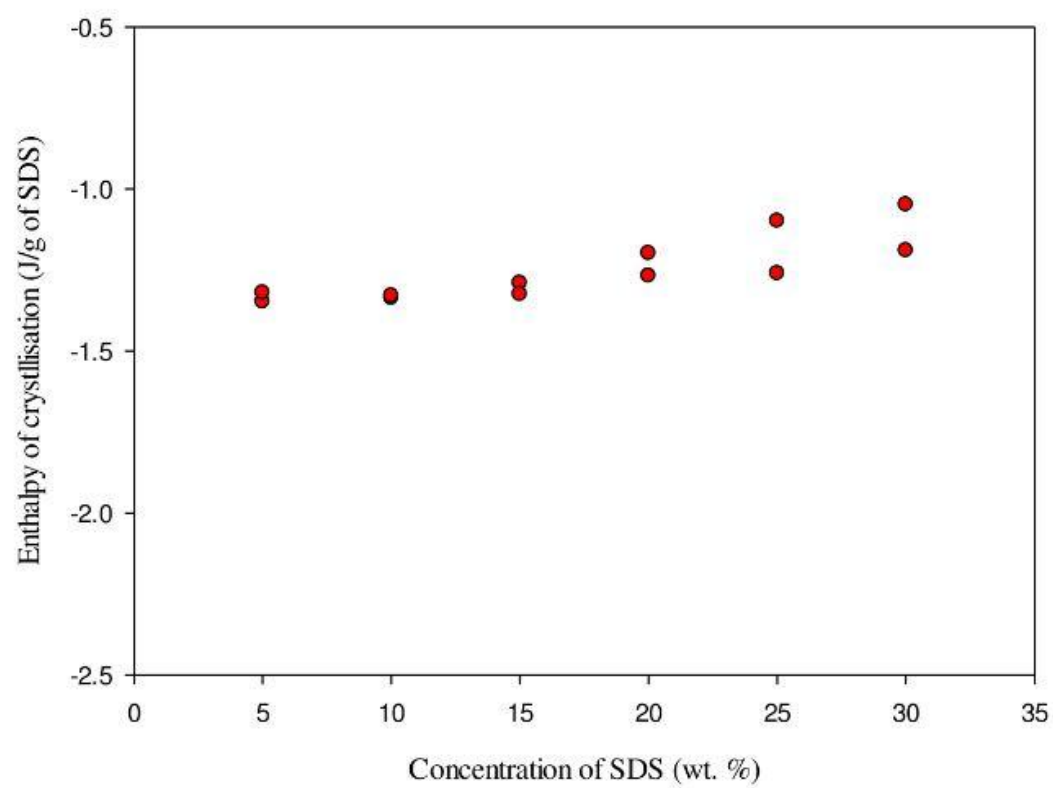


Fig 4

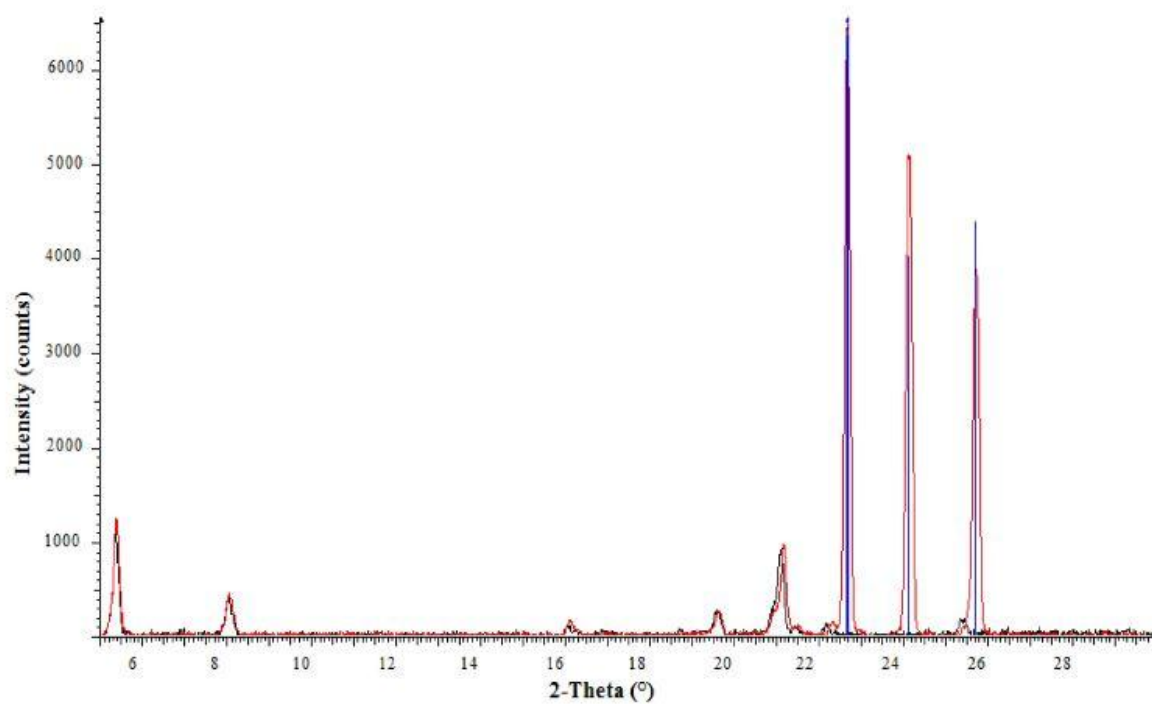


Fig 5a

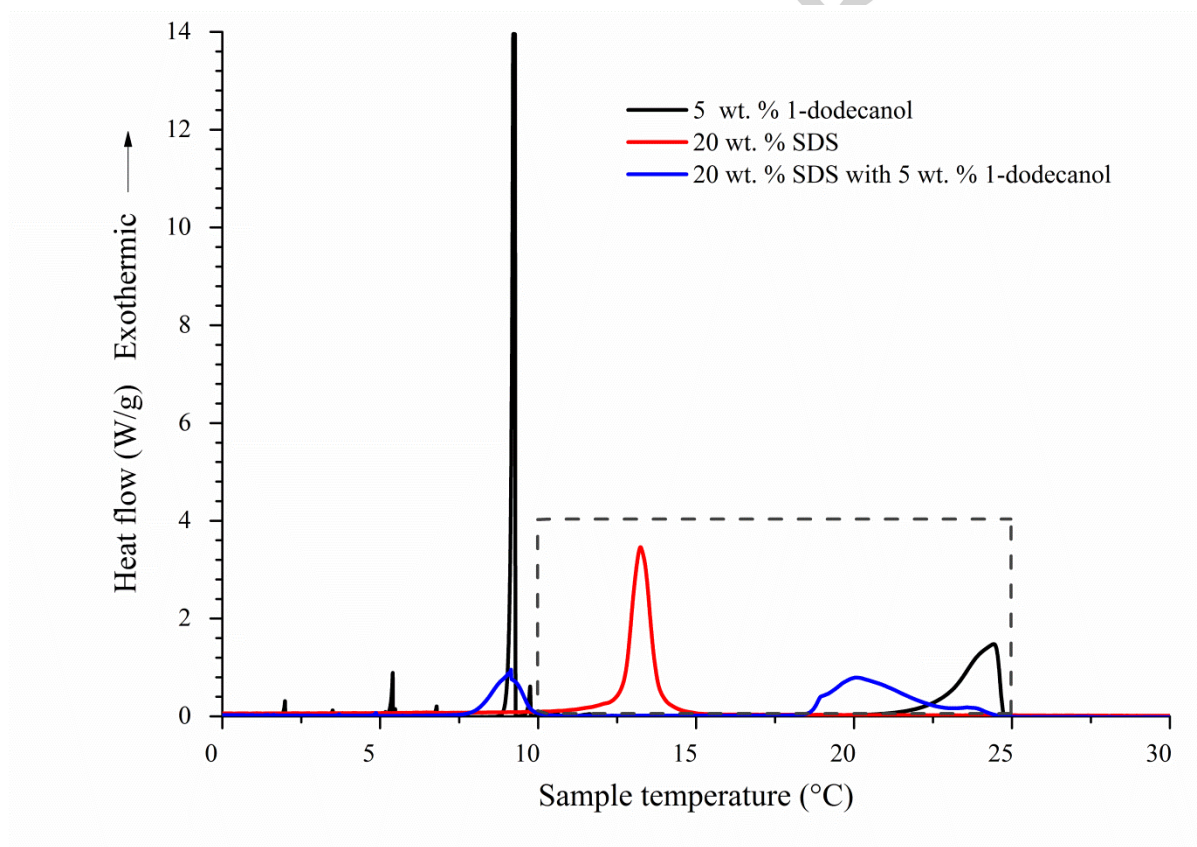


Fig 5b

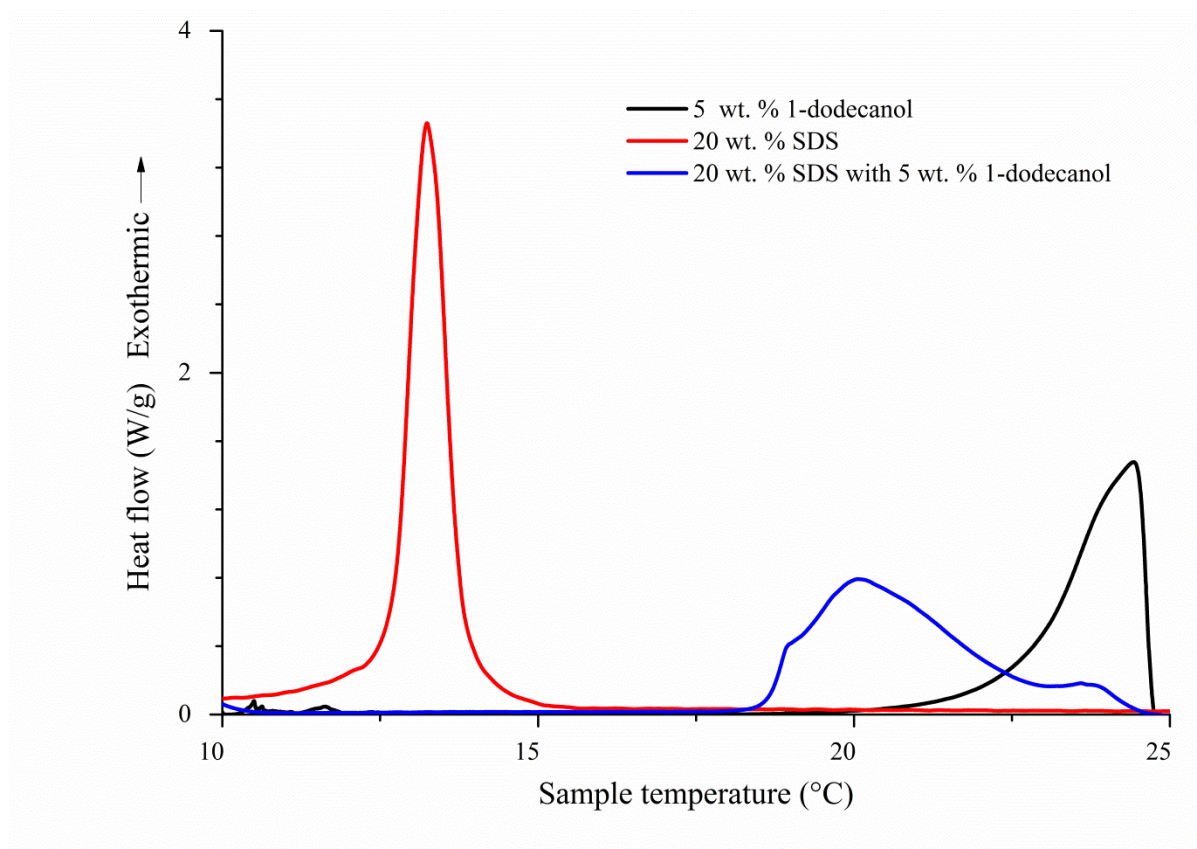


Fig 6

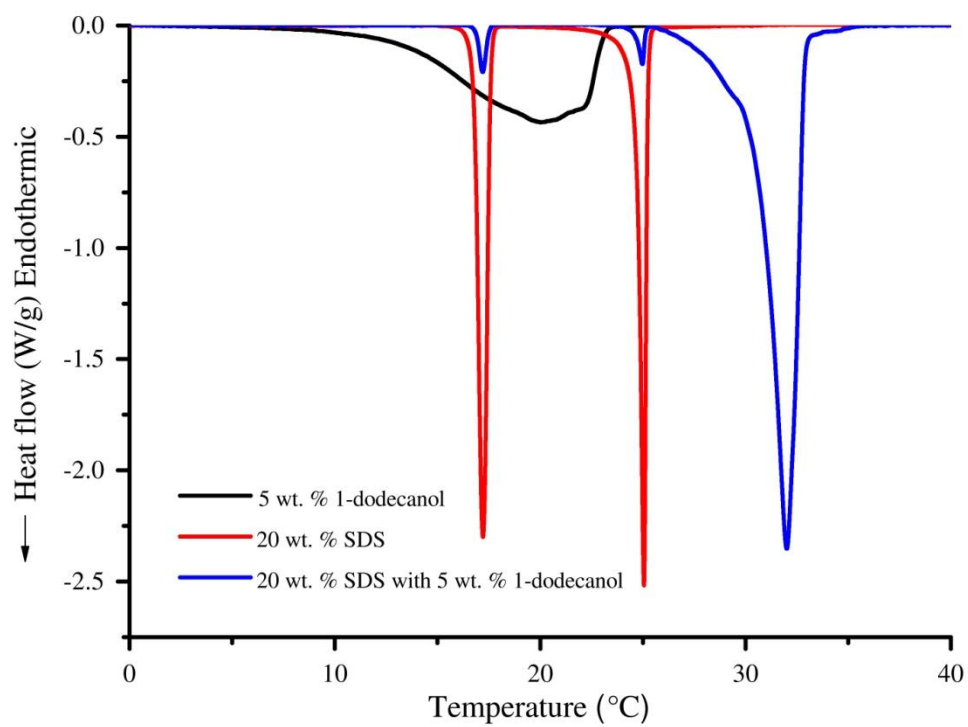
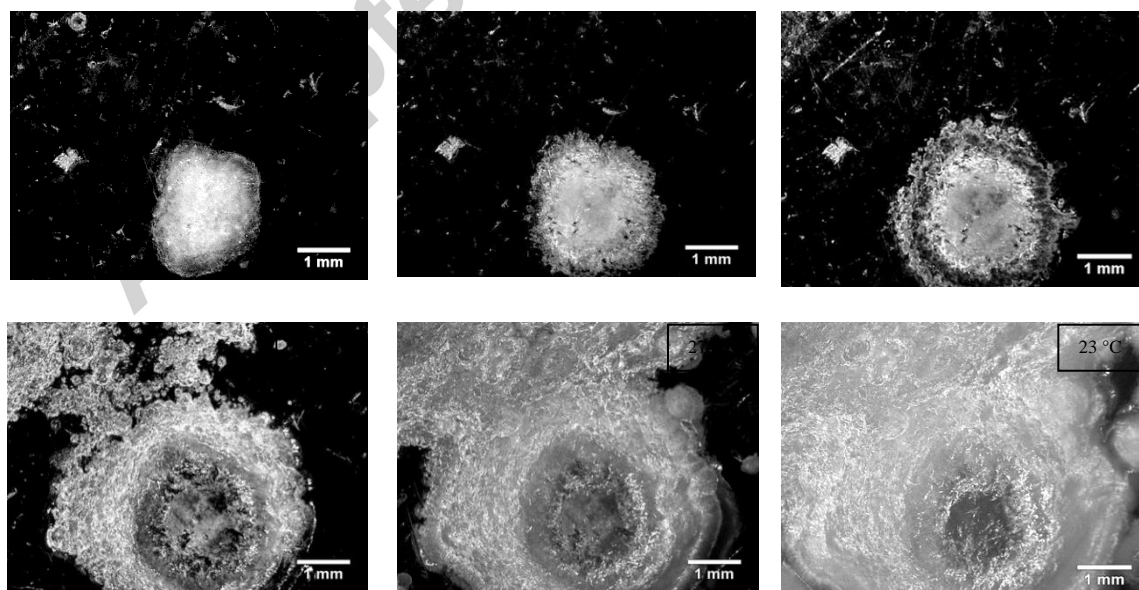


Fig 7



Highlights

- At low temperatures, surfactant crystallisation can occur in liquid detergents
- Crystallisation of SDS with respect to concentration variability is discussed
- 1-dodecanol is shown to facilitate SDS crystallisation

Accepted manuscript