J Am Oil Chem Soc (2008) 85:413–419
DOI 10.1007/s11746-008-1216-z

ORIGINAL PAPER

# Surface Melting in Alkane Emulsion Droplets as Affected by Surfactant Type

**İbrahim Gülseren · John N. Coupland**

Received: 19 October 2007 / Revised: 26 December 2007 / Accepted: 15 February 2008 / Published online: 7 March 2008

**Abstract** The influence of surfactant type (Tween 20, Tween 40, Tween 60, Tween 80, Brij 58, Triton X-100, SDS, STS) on the crystallization and melting characteristics of emulsified (mean droplet diameter 0.52 μm) *n*-octadecane and *n*-eicosane were studied using microcalorimetry. The melting point (~37 °C) of the eicosane droplets was higher than the crystallization point (~24 °C) and was not affected by the surfactant selected. There was a similar separation between the crystallization (~14 °C) and melting (~28 °C) point of the emulsified octadecane however the details of the transitions was affected by the surfactant selected. For Tween 40 and Brij 58-stabilized droplets there was a split peak on crystallization which we attribute to a surface heterogeneous nucleation mechanism. Only these surfactant-alkane combinations had a split peak on melting. The size of the lower temperature fraction decreased with droplet size suggesting another surface effect. However, the size of the surface layer was calculated to be many times the length of the surfactant tail suggesting the crystal structure was modified by the nucleation mechanism.

**Keywords** Surface melting · *n*-Alkane · Emulsions · Surfactants

## Introduction

The thermodynamic melting point of an alkane is determined by the balance between the intermolecular bonds broken (i.e., enthalpy loss) and loss of order (i.e., entropy gain) in moving from a crystalline to a liquid state. The thermodynamic crystallization temperature is determined by the same factors but is frequently kinetically limited by the need to form a crystal nucleus and is consequently observed at a lower temperature than melting. The magnitude of supercooling in alkanes is much greater when the lipid is present in fine emulsion droplets where each droplet must nucleate independently.

Crystal nucleation in emulsified droplets is also affected by the interfacial surfactant material present. Surfactants that have similar alkyl chain lengths as the emulsified lipid have been shown to increase the crystallization point of emulsion droplets, presumably by ordering the lipid adjacent to the surface and reducing the barrier to nucleation [1, 2]. Alternatively, surface crystallization of the surfactant itself can facilitate nucleation in the lipid contained [3] which may be seen as a small endothermic peak in a differential scanning calorimetry thermogram immediately before the major lipid crystallization peak [4]. On the other hand, Povey et al. [5] suggested that the surfactant tail groups act as an impurity in the lipid close to the surface and can hence lower the crystallization temperature of that portion of the fat. In all cases the magnitude of any surface effects increases with decreases in droplet size.

In most investigations the influence of surfactants on droplet lipid melting has been found to be minimal, since at reasonably slow heating rates, melting occurs at the thermodynamic melting point [2]; there are however some exceptions to this rule. First, the higher Laplace pressure in very fine droplets has the effect of lowering their melting point [6] although for this effect to be significant the droplets would have to be considerably smaller than typical macroemulsions (i.e., possibly <0.5 μm, [7]). Secondly, the surface crystalline lipid is present in a mixture with the

---

İ. Gülseren · J. N. Coupland (✉)
Department of Food Science, The Pennsylvania State University,
337 Food Science Building, University Park, PA 16801, USA
e-mail: coupland@psu.edu; Coupland@psu.edu

hydrophobic moieties of the surfactant and is hence a less pure material and should therefore have a lower melting point than similar crystalline lipids in the core of the droplet. There have been limited experimental investigations of this hypothesis but recently, Povey et al. [5] were able to use ultrasonic velocity measurements to detect differences in the melting transition due to changes in the surfactant.

The goal of the present work is to investigate the effects of lipid-surfactant interfacial interactions on the melting behavior of lipids. We use microcalorimetry to make careful measurements of the melting (and crystallization) transitions in emulsified alkanes as a function of droplet size and surfactant type and conclude that the lipid closest to the surface will melt before the core lipid if it is compatible with the hydrophobic portion of the surfactant.

## Materials and Methods

### Materials and Sample Preparation

*n*-Octadecane ($C_{18}$ >99%) and *n*-eicosane ($C_{20}$, 99%) were obtained from Acros Organics (Morris Plains, NJ). Tween 20, Brij 58, and Triton X-100 were purchased from Sigma Aldrich Chemical Company (St. Louis, MO). Tween 40 and Tween 60 were obtained from MP Biomedicals, Inc (Solon, OH). Sodium tetradecyl sulfate (STS) solution (27%) was purchased from Pfaltz & Bauer, Inc (Waterbury, CT). Tween 80 and sodium dodecyl sulfate (SDS) were purchased from Fisher Scientific (Pittsburgh, PA).

To prepare the emulsions, varying amounts of alkane and surfactant were mixed with water at 50 °C (to ensure the lipid was liquid during homogenization), stirred for 30 min and emulsified using a 250 W ultrasonic processor (Vibracell, Sonics & Materials, Danbury, CT, USA) equipped with a stainless steel probe (½ in) at the highest power setting with a 50% duty cycle. The process time was adjusted (<2.5 min) to produce emulsions with a mean diameter ($d_{32}$) of 0.52 ± 0.01 μm.

The particle size distribution of the emulsions was characterized by static light scattering (Horiba LA-920, Irvine, CA, USA) after appropriate dilution. The emulsions were stable over the course of the experiment (i.e., no change in particle size, no visible phase separation) and were not destabilized by the cooling-heating cycles which lasted approximately 8 h for $C_{18}$ samples and 9 h for $C_{20}$ samples. A fraction of the samples were kept at room temperature and under refrigeration for 2 weeks and no visible separation or changes in particle size were observed. The emulsions were diluted in water to produce a final oil concentration of 0.25% and surfactant concentration of 1%. If necessary, the samples were heated before the sonication procedure in order to keep the oil in a liquid state.

In another series of experiments, octadecane emulsions with a wider mean particle size range (0.19–5.58 μm) were prepared using Tween 40. For the preparation of these samples, in addition to the ultrasonic processor, a high speed blender (Kinematica GmbH FT10/35, Brinkmann Instruments, Switzerland) and a two-stage valve homogenizer (1–5 passes, 200–600 bar, 10% of which was maintained over the second stage, Niro-Soavi Panda, Model no: 3344, Parma, Italy) were used as necessary. In order to keep the oil in a liquid state for homogenization, the homogenizer was preheated with hot water prior to use.

### Differential Scanning Calorimetry

The crystallization and melting thermograms were measured using differential scanning calorimetry (VP-DSC, Microcal, Northampton, MA). Samples diluted to 0.25 wt% lipid with water prior to analysis were used so that the signals were within the range of the instrument. Samples (513.1 μl) were run against a similar reference cell filled with water. $C_{18}$ and $C_{20}$ samples were heated to 35 and 45 °C, respectively, held for 30 min, and cooled to 0.5 °C at 10 °C $h^{-1}$ then held for a further 30 min and reheated at the same rate to 35, and 45 °C for $C_{18}$ and $C_{20}$ samples. The heat capacity data for the water-water scan was subtracted from the sample runs to measure the heat flux due to changes in the lipid phase. In preliminary experiments, we showed that the surfactant solutions did not themselves show any measurable thermal transitions over this range.

## Results and Discussion

### Crystallization

The cooling thermograms of eicosane emulsions (0.25 wt% o/w, 0.52 μm) stabilized by various surfactants are shown in Fig. 1. The calorimetry was extremely reproducible with typical standard deviations in onset and peak temperature of 0.1 and 0.2 °C, respectively. All small-molecule surfactant stabilized eicosane samples crystallized with a characteristic double peak with the larger portion having an onset at about 24 °C and the minor portion at 20.5 °C. The major peak in all samples was tentatively attributed to the formation of the rotator phase (R) and the minor one to the transition of the rotator phase (R) to the low temperature crystalline phase (LO) [8, 9]. For all samples, the major peak was about 15 °C below the thermodynamic melting point of octadecane (i.e., 28.2 °C, [10]). Interestingly, the nucleation of eicosane was not affected by the surfactant used with the exception of SDS

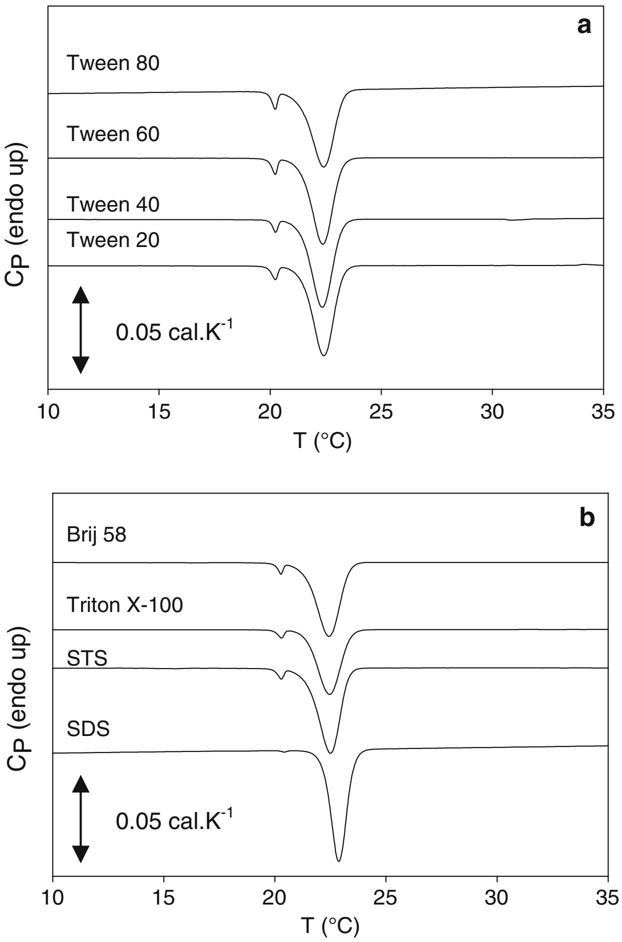

**Fig. 1** Cooling thermograms of 0.25% *n*-eicosane emulsions stabilized by **a** Tween emulsifiers (1%), **b** non-Tween emulsifiers (1%) recorded at a scanning rate of 10 °C $h^{-1}$. The mean particle size ($d_{32}$) for all samples is 0.52 µm

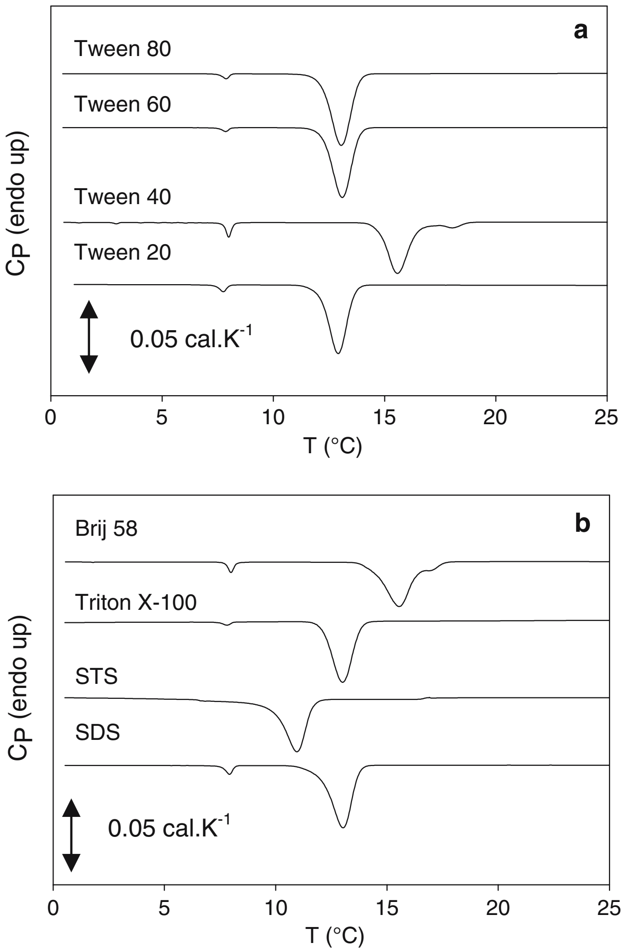

**Fig. 2** Cooling thermograms of 0.25% *n*-octadecane emulsions stabilized by **a** Tween emulsifiers (1%), **b** non-Tween emulsifiers (1%) recorded at a scanning rate of 10 °C $h^{-1}$. The mean particle size ($d_{32}$) for all samples is 0.52 µm

stabilized samples. At this time, we are not certain about the nature of the interaction between SDS and eicosane.

In our earlier work [9] we reported similar thermograms for emulsions of hexadecane, octadecane and eicosane stabilized with either Tween 20 or sodium caseinate. In that work we pointed to the minor peak in the eicosane samples at 20.5 °C as the crystallization of a surface layer immediately following the larger crystallization peak of the core of the droplet. In the light of the larger data set available in this work we now believe this attribution was incorrect and the minor peak is indeed a rotator to crystal phase transition in the lipid. All samples showed a peak at approximately the same temperature although the peak size was somewhat different. Our previously published discussion [9] may be particularly confusing as the zoom shown in Fig. 4b of that work focuses on the wrong temperature range.

Similar experiments were conducted using octadecane droplets stabilized by the same range of surfactants (Fig. 2). For most surfactants used there was a single exothermic peak with a maximum at 12.7 °C (i.e., Tween 80, Tween 60, Tween 20, Triton X-100, SDS). Other surfactants had a similar peak at a higher temperature (~16 °C, Tween 40 and Brij 58) and the exothermic peak for this group overlapped with another small exothermic transition at still higher temperatures. One surfactant, STS, had a lower crystallization peak (11 °C maximum). There was a small but reproducible exothermic peak at 7 °C in all emulsions except those prepared with STS where it may not have been evident because it overlapped with the long tail on the major peak. At present we can offer no good mechanism for the low crystallization onset of the STS samples.

The major peak in all samples was tentatively attributed to the formation of the rotator phase (R) and the minor one (i.e., 7 °C for octadecane) to the rotator phase (R) to low temperature crystalline phase (LO) transition [8, 9]. For all samples the major peak was about 15 °C below the thermodynamic melting point of octadecane. The two samples crystallizing at higher temperatures (i.e., Brij 58 and Tween 40) may have had their nucleation catalyzed by the presence of the surfactant. The ability of a surfactant layer to catalyze nucleation in emulsion droplets has been widely observed (e.g., McClements et al. [2]) and is usually attributed by an ordering of the surface lipid by the oriented surfactant molecules at the interface. According to McClements et al. [2], when the lipid and surfactant tail had a similar carbon number they would be compatible and the droplet would tend to crystallize at a higher temperature. The alkyl chain length for the Tween surfactants are 12, 16 and 18 carbons for Tween 20, Tween 40, and Tween 60, respectively so according to the McClements theory we would expect the crystallization temperatures of the Tween 60-stabilized emulsion to be highest. However in our work, Tween 40-stabilized octadecane droplets had the highest crystallization temperature while Tween 60 and Tween 20-stabilized droplets were lower and similar to one another. The lower compatibility of Tween 60 is possibly due to its longer alkyl chain length (i.e., >16 carbons) which lowers the efficiency of adsorption due to coiling of the surfactant molecule [11].

Other workers using less-sensitive calorimetric methods have not reported the double peak associated with surface-catalyzed nucleation (i.e., Tween 40 and Brij 58 samples). We suggest that the small peak at high temperatures is due to the crystallization of a surface layer adjacent to the surface. Once formed, the surface crystals rapidly nucleate the core lipid and give rise to the larger peak. In the lower-onset samples (i.e., Tween 80, Tween 60, Tween 20, Triton X-100, SDS) there is effectively one population of lipid droplets unaffected by the surface material. Nucleation occurs somewhere in the bulk of the droplet and the crystal grows from there. It is striking that the minor peak (at 7 °C) that we tentatively assigned to a rotator to crystal phase transition is unaffected by the presence of the surface layer, even in those samples where the surfactant could catalyze a liquid to rotator transition. The minor transition must therefore initiate in the bulk of the lipid droplet for all samples.

An alternative explanation of the split-peak and higher onset of the Tween 40 and Brij 58 samples would be that a phase transition in the surfactant catalyzed the nucleation of the droplets (see reference [5] for a similar argument using a high-melting hydrophobic surfactant). However we were not able to detect any thermal events in solutions of the surfactant suggesting that some interaction involving the octadecane must be important.

## Melting

The heating thermograms of eicosane emulsions (0.25 wt% o/w, 0.52 μm) stabilized by various surfactants are shown in Fig. 3. The calorimetry was extremely reproducible with typical standard deviations in onset and end point temperature of 0.1 and 0.3 °C, respectively. There was a large, unimodal, endothermic peak independent of surfactant type with an end point of approximately 37 °C corresponding to the thermodynamic melting point of these lipids (36.9 °C, [10]). Figure 3 shows a 15–40 °C range of the thermograms and reveals a minor peak at 25 °C for all samples. While not clearly visible on the scale of the main figure, the higher resolution zoom (5% o/w emulsions) to Fig. 3 shows the 0–30 °C region. We have previously identified this peak in eicosane as a crystal to rotator phase transition [9]. Once again the solid-solid transition is unaffected by the surfactant. STS samples were observed to have an additional peak approximately around 13.5 °C.

The major melting endothermic peak for the octadecane samples was typically more complex, however the end temperature (approximately 28 °C) corresponds well with the thermodynamic melting point (28.2 °C, [10]) (Fig. 4). Once more, there was a very minor peak at 15 °C shown in the zoomed region (0–20 °C) of Fig. 4 which we attribute to a crystal to rotator phase transition for most of the small-molecule surfactant that were investigated here, mainly for Tween 40 and Brij 58.

There are clear parallels in the details of the major melting transitions with the groupings seen in the crystallization behavior of the same systems. The samples that crystallized with a single peak at the lower temperatures (i.e., Tween 80, Tween 60, Tween 20, Triton X-100, SDS) had a bimodal melting transition (minor peak at low temperatures, major peak at high temperatures). The samples with higher crystallization temperatures (i.e., Tween 40 and Brij 58) had at least one more peak in the melting transition suggesting there were several populations of lipid going through transitions. The STS samples are an outlier with a lower melting point and a low crystallization point than the other surfactants studied.

Calorimetric studies of alkane droplet melting have rarely shown anything but a single transition. However some workers have suggested there may be two populations of lipid present in a crystalline droplet—a core of "pure" material and a surface layer contaminated with the hydrophobic tails of the surfactant. For example, Walstra and van Beresteyn [12] suggested there should be a reduction in the melting point of emulsified lipids if the emulsifiers act as impurities in the lipid phase. Povey et al. [5] used sensitive ultrasonic velocity measurements to show that the onset of melting in hexadecane droplets occurred several degrees below the thermodynamic melting point and attributed this to an interaction with the hydrophobic tails of the Tween 20 surfactant used [3].

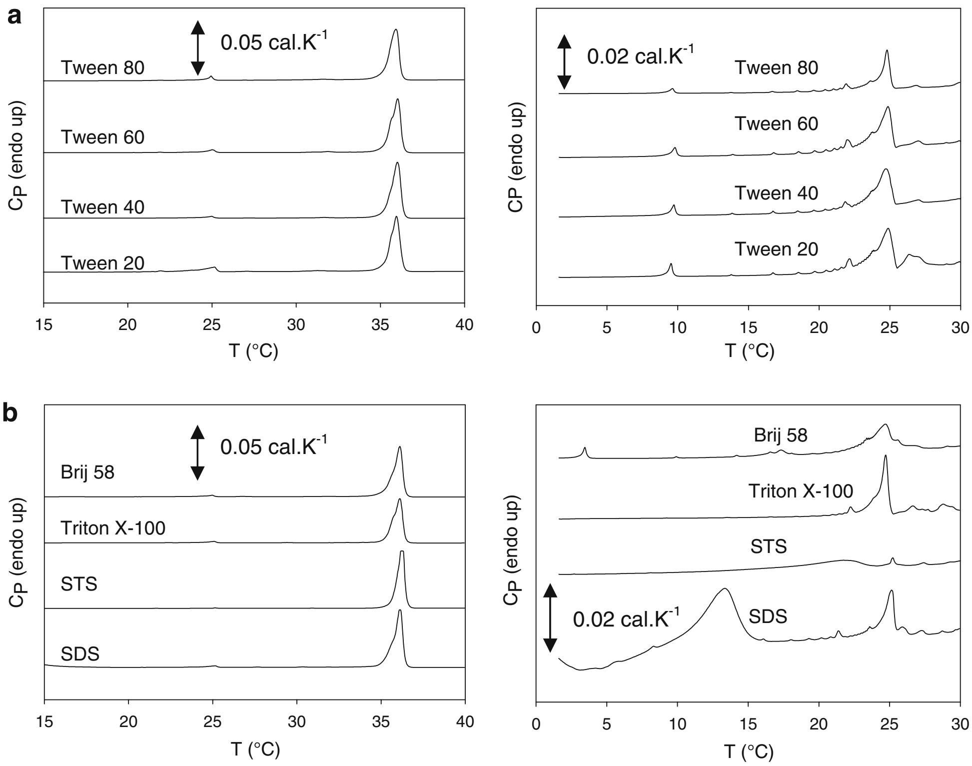

**Fig. 3** Heating thermograms of 0.25% *n*-eicosane emulsions stabilized by **a** Tween emulsifiers (1%), **b** non-Tween emulsifiers (1%) recorded at a scanning rate of 10 °C $h^{-1}$. The figures to the *right* are the higher resolution zooms (5% emulsion) of the main data sets shown on the *left*. The mean particle size ($d_{32}$) for all samples is 0.52 μm

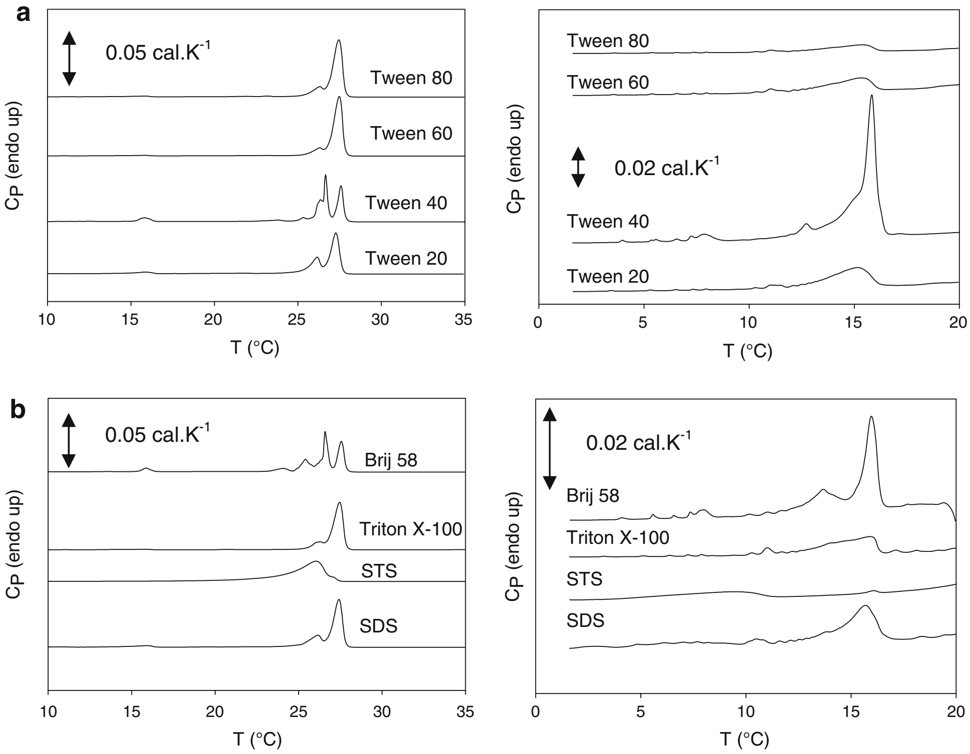

**Fig. 4** Heating thermograms of 0.25% *n*-octadecane emulsions stabilized by **a** Tween emulsifiers (1%), **b** non-Tween emulsifiers (1%) recorded at a scanning rate of 10 °C $h^{-1}$. The figures to the *right* are the higher resolution zooms (5% emulsion) of the main data sets shown on the *left*. The mean particle size ($d_{32}$) for all samples is 0.52 μm

## Surface Effects on Droplet Melting

A novel finding of this work is the details of both the melting and crystallization of alkane droplets depend on an interaction between the lipid and surfactant. Phase transitions in eicosane droplets are relatively simple and not affected by the surfactant while crystallization in octadecane droplets, presumably because the hydrophobic tails of the surfactant are closer in size to the lipid molecules, is strongly affected. Although only some surfactants (i.e., Tween 40 and Brij 58, both of which have a $C_{16}$ tail length) can catalyze octadecane droplet nucleation and lead to a split and higher crystallization peak, all samples studied had a split peak in melting. If we assume the surfactant is functional at the droplet surface then the proportion of the total melting enthalpy at the lower temperatures should decrease with droplet size (specific surface area).

To test this hypothesis, we measured the crystallization and melting thermograms of a range of Tween 40-stabilized octadecane emulsions with the same composition but different droplet sizes. The size of the lower temperature crystallization peak (data not reported) and the high-temperature melting peak increased with droplet size (Fig. 5a). This effect can be seen more systematically by dividing the enthalpy into two populations by simply drawing a construction line to the baseline from the minima between the high and low melting peaks (Fig. 5b, a similar approach was taken for the crystallization transition but these data are more generally understood and are not reported). This general trend of the surface-affected fraction increasing with decreasing droplet size is expected and, according to this approach, the surface melting fraction (SM%) can be calculated from DSC thermograms:

$$\mathrm{SM}(\%) = \frac{A_{\mathrm{molten}}}{A_{\mathrm{molten}} + A_{\mathrm{core}}} \times 100 \tag{1}$$

where $A$ represents area under the DSC melting curve (Fig. 5c) for the molten phase and the droplet core as indicated by the corresponding indices. How does this model correspond to the size of the real structures involved? A highly schematic model of a small droplet surrounded by a layer of surfactant is provided in Fig. 5d [5]. The measured diameter of the droplet is given by $D$. The size of the surfactant headgroup is relatively small (for Tween 20 ~1.4 nm [13]) so this can be taken as the size of the lipid phase itself. The lipid phase is divided into two volumes: the inner oil (diameter $d$) is effectively pure and its contribution to the surface melting enthalpy would correspond to $A_{\mathrm{core}}$ above while the section closest to the interface is affected by the surfactant and corresponds to $A_{\mathrm{molten}}$ above. Accounting for the density changes associated with the phase transition the surface melting fraction can be expressed in terms of the geometry of this model:

$$\mathrm{SM}(\%) = \frac{D^3 - d^3}{d^3} \cdot \frac{\rho_{\mathrm{liquid}}}{\rho_{\mathrm{crystal}}} \times 100 \tag{2}$$

where, $\rho$ is the density of the subscripted alkane phase. The distance $(D\text{-}d)/2$ is the thickness of the surface layer and for

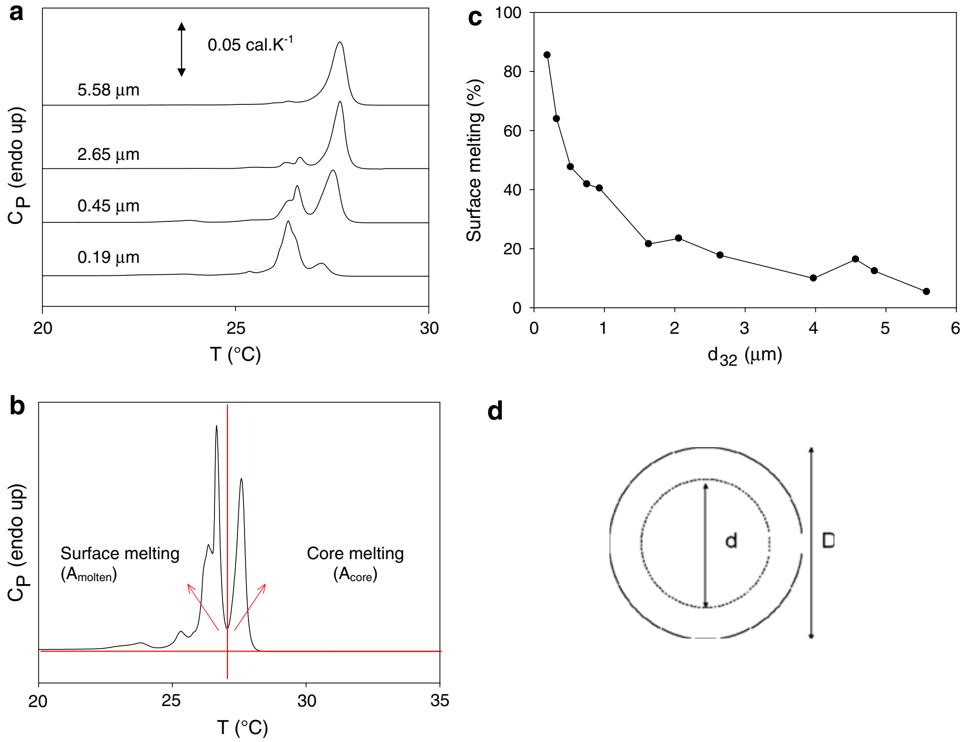

**Fig. 5** **a** Heating thermograms of 0.25% *n*-octadecane emulsions stabilized by Tween 40 (1%) as affected by the particle size (0.19 µm to 5.58 µm). **b** Illustration of the constructions used to divide the peak on the thermogram into: "surface" and "bulk" components. **c** A simple physical model of a droplet (diameter *D*) with a pure lipid core (diameter *d*). **d** The surface melting (%) characteristics of 0.25% *n*-octadecane emulsions stabilized by Tween 40 (1%) as affected by the particle size (0.19 µm to 5.58 µm)

melting of *n*-octadecane droplets (Fig. 5c) this value increased with droplet diameter (from 44 nm when the mean particle size ($d_{32}$) was 190 nm, to 195 nm for the droplets with a mean particle size of 4,840 nm. (Considering the full size distribution function instead of just the mean values made little difference to these calculations). Povey et al. [5] proposed that the thickness of the surface layer would correspond to the length of the hydrophobic portion of the surfactant acting as a contaminant in the surface oil (~4 nm for Tween 40 [14]). Clearly the actual surface values are much larger and droplet size dependent. While the chemistry of the surfactant is important, its influence extends much further into the droplet than the physical size of the molecule.

An alternative explanation may be that differences in the nucleation pattern lead to differences in droplet melting. We have argued that the emulsions showing a significant, size dependant double peak on melting were those whose crystallization was itself catalyzed at the surface (i.e., Brij 58 and Tween 40-stabilized octadecane). It could be that because these lipids nucleate from the impure surface layer, the structure of the crystals formed is different than the structure of the crystals formed by from nucleation in pure alkanes. The different crystal structure would propagate further into the core of the droplet than the physical size of the surface layer and could explain the relatively large surface thickness from our earlier calculations. A second contributing factor could be the physical constraints imposed on crystal structure by the droplet surfaces. It is well-known that the confinement of oil molecules in droplets can alter the polymorphic behavior [6, 15] and cause defects in crystal structure when nucleation activating impurities are present [16].

## Conclusions

The melting and crystallization of emulsified eicosane is largely unaffected by the surfactant selected while similar octadecane droplets can show an additional high temperature crystallization transition and low temperature melting transition with certain surfactants (Brij 58 and Tween 40). We propose that these surfactants are molecularly compatible with the lipid and can catalyze nucleation from the droplet surface. The crystals nucleating at the surface have somewhat different structures and therefore melting properties than the crystals nucleating in the bulk of the droplet.

**Acknowledgments** The project was supported by the National Research Initiative of the USDA Cooperative State Research, Education and Extension Service, grant number 2003-35503-13852.

## References

1. Skoda W, van den Tempel M (1963) Crystallization of emulsified triglycerides. J Colloid Sci 18(6):568–584
2. McClements DJ, Dungan SR, German JB, Simoneau C, Kinsella JE (1993) Droplet size and emulsifier type affect crystallization and melting of hydrocarbon-in-water emulsions. J Food Sci 58(5):1148–1151, 78
3. Kaneko N, Horie T, Ueno S, Yano J, Katsuragi T, Sato K (1999) Impurity effects on crystallization rates of n-hexadecane in oil-in-water emulsions. J Cryst Growth 197(1–2):263–270
4. Awad TS, Sato K (2002) Fat crystallization in o/w emulsions controlled by hydrophobic emulsifier additives. In: Marangoni AG, Narine SS (eds) Physical properties of lipids, Marcel Dekker, USA
5. Povey MJW, Hindle SA, Aarflot A, Hoiland H (2006) Melting point depression of the surface layer in n-alkane emulsions and its implications for fat destabilization in ice cream. Cryst Growth Des 6(1):297–301
6. Montenegro R, Landfester K (2003) Metastable and stable morphologies during crystallization of alkanes in miniemulsion droplets. Langmuir 19(15):5996–6003
7. Montenegro R, Antonietti M, Mastai Y, Landfester K (2003) Crystallization in miniemulsion droplets. J Phys Chem B 107(21):5088–5094
8. Gülseren İ, Coupland JN (2007a) Excess ultrasonic attenuation due to solid-solid and solid-liquid transitions in emulsified octadecane. Cryst Growth Des 7(5):912–918
9. Gülseren İ, Coupland JN (2007b) The effect of emulsifier type and droplet size on phase transitions in even emulsified n-alkanes. J Am Oil Chem Soc 84(7):621–629
10. Vargaftik NB (1975) Tables on the thermophysical properties of liquids and gases: in normal and dissociated states. Hemisphere Publishing Comp, USA
11. Rosen MJ (1989) Surfactants and interfacial phenomena. 2nd edn. Wiley, USA
12. Walstra P, van Beresteyn ECH (1975) Crystallization of milk fat in the emulsified state. Neth Milk Dairy J 29(1):35–65
13. Mandal AB, Gupta S, Moulik SP (1985) Characterization of Tween 20 and Tween 80 micelles in aqueous-medium from transport studies. Indian J Chem A 24(8):670–673
14. Sato K, Ueno S (2001) Molecular interactions and phase behavior of polymorphic fats. In: Garti N, Sato K (eds) Crystallization processes in fats and lipids. Marcel Dekker Inc., New York, pp 177–210
15. Ueno S, Hamada Y, Sato K (2003) Controlling polymorphic crystallization of n-alkane crystals in emulsion droplets through interfacial heterogeneous nucleation. Cryst Growth Des 3(6):935–939
16. Sonoda T, Takata Y, Ueno S, Sato K (2006) Effects of emulsifiers on crystallization behavior of lipid crystals in nanometer-size oil-in-water emulsion droplets. Cryst Growth Des 6(1):306–312