UNIVERSITY OF LEEDS

Quasi isothermal crystallization kinetics, non-classical nucleation and surfactant dependent crystallization

Malcolm Povey, Tarek Awad, Ran Huo and Yulong Ding, University of Leeds

Classical Nucleation theory

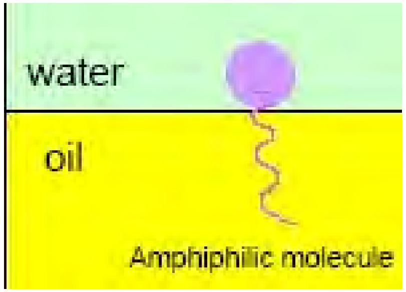
Turnbull 1950s Applied to metals and n-hexadecane

Kloek, Walstra, van Vliet Applied to triacylglycerols

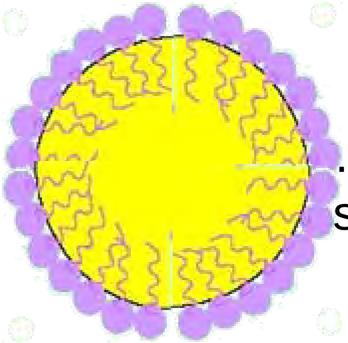
- Volume homogeneous nucleation, volume heterogeneous nucleation, surface heterogeneous nucleation

But does this work in micro- and nano-emulsions?

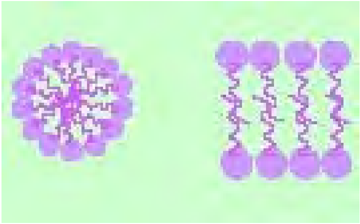
Effect of surfactant



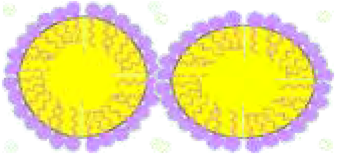
…not the same as



…not the same as



…not the same as



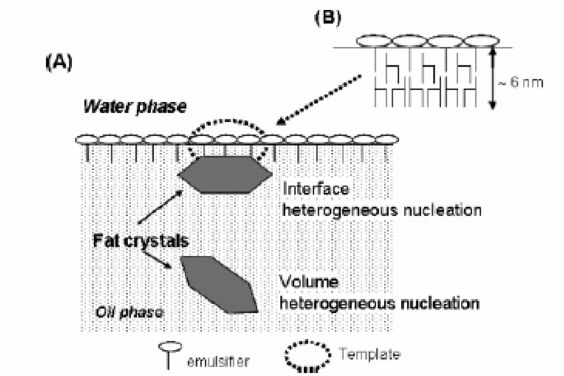
Surface nucleated crystallization

Polymorphic modification of crystal

Comminution affects the structure of the surfactant in the continuous phase and at the interface

Melting point depression of droplet surface layer

‘Microemulsion’ phenomena



Sonada et al, Crystal Growth & Design 2006, 6, 306-312

Comminution and surfactant

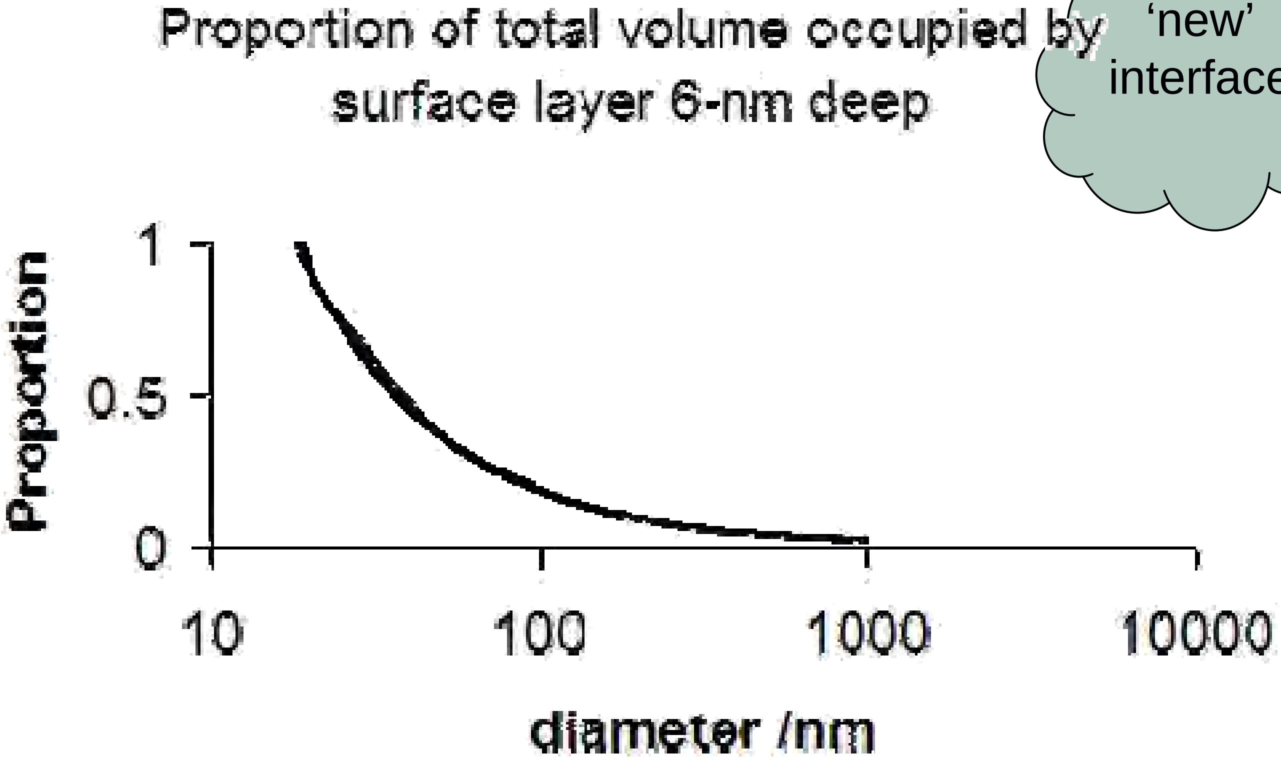
Reducing size increases the proportion of molecules in contact with the surface

The surface molecules are ‘mixed’ with surfactant

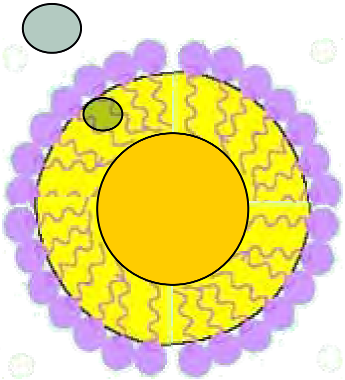
Surface energy terms come to dominate the total particle energy

Thermodynamics are altered

One particle becomes a particle and a ‘shell’ of surfactant dissolved in the bulk phase



Proportion of total volume occupied by surface layer 6-nm deep



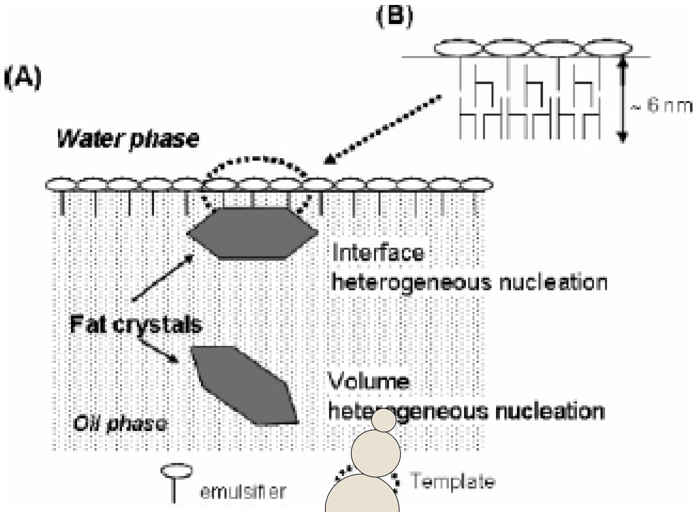
What other effects of size reduction?

The probability of finding a critical crystallization nucleus or catalytic impurity in the volume of an emulsion oil particle falls to zero.

Something else must induce crystallization, however, the crystallization temperature is not particularly dependent on surfactant.

We had presumed that crystallization would be controlled by surface heterogeneous nucleation by surfactant.

The surfactant is important but it does not behave like an ordinary nucleator.



Sonada et al. C l Growth & Design 2006, 6, 3

Does this apply as particle size falls?

We study monodisperse emulsions

Polydispersity makes it more difficult to study crystallization kinetics.

Monodispersity

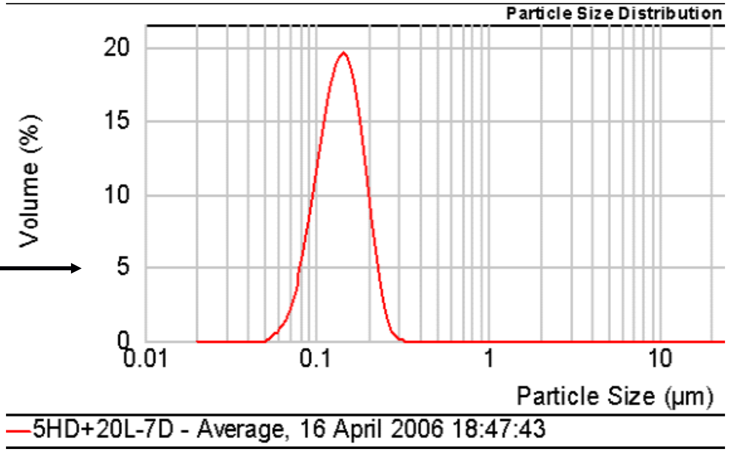
(a) Stabilises the emulsion

- eliminate depletion flocculation
- minimise Ostwald ripening

(b) Controls crystal size, shape and polymorphic form

(c) Minimise the concentration of surfactant in the continuous phase using high pressure homogenisation – further reduces Ostwald ripening

In all our experiments we achieve a given particle size and distribution using a variety of surfactants. We can then study the effect of BOTH particle size and surfactant



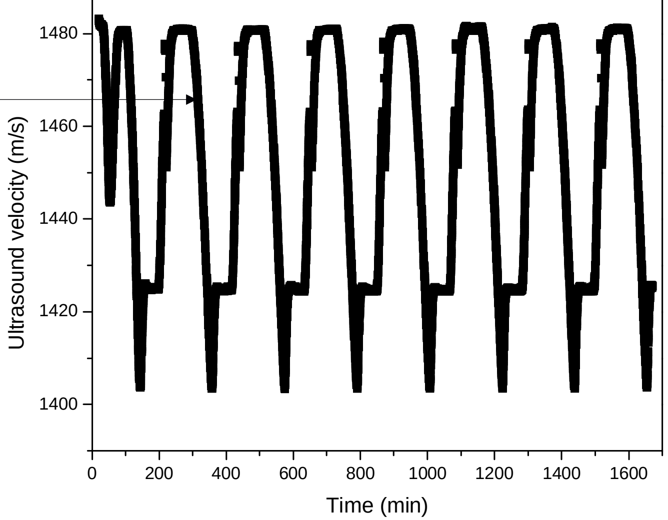
We use ultrasound to determine crystal content

Velocity of sound measured against time as the emulsion is cycled from 0C to 40C. The n-hexadecane emulsions are very stable.

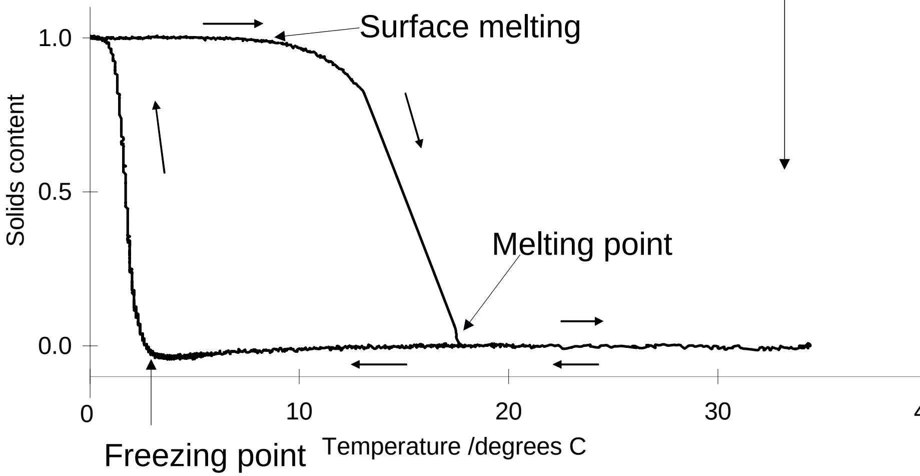
Volume fraction occupied by solid material can be calculated from the velocity measurements.

Solid content in the dispersed phase (20 %v/v) can be determined from the sound velocity with an accuracy of 1% and precision ten times better than that. This scales with volume fraction.

Our first requirement – a stable, monodisperse emulsion. Use 130 nm, n-hexadecane in water, with 1% Tween 20.



$$v = 1/\sqrt{\kappa \cdot \rho}$$



DSC and velocity determined solids

Ultrasound velocity can determine solids content without changing temperature.

Temperature change is essential to generate the necessary heat flow in the case of DSC.

Therefore ultrasound can operate at very low or zero temperature scanning rates.

How to interpret ultrasound velocity data?

$\Delta S = \Delta H / T_m$

Generalised nucleation kinetics

$$\frac{Nk_B}{h}\exp\left(-\frac{\alpha\Delta S}{R}\right)\exp\left(-\frac{\Delta G^*}{k_B T_{abs}}\right) = \frac{J}{T_{abs}} = \frac{k_x}{L^x T_{abs}}$$

J is the nucleation rate for crystallisation;

N is the number density of catalytic impurities, k_B is Boltzmann's constant; *h* is Plank's constant;

the probability that a fraction *α* of the molecule is in the right conformation to crystallise; *R* is the gas constant;

$\Delta S = \Delta H/T_m$ the loss of entropy on incorporation of material in a nucleus where *T*m is the melting temperature and *ΔG** is the Gibbs activation energy for the formation of a spherical nucleus; *ΔH* is the enthalpy of fusion.

To account for the penetration of the surfactant into the bulk of the droplet we allow the possibility of both surface and volume nucleation occurring.

Therefore an arbitrary dimensionality *x is* introduced which is 2 for surface nucleation and 3 for volume nucleation and *L* is a length, corresponding to diameter for spheres. A correspondingly appropriate nucleation rate constant *k*x is required.

Collision mediated nucleation

Determine k_s from the slope against time of

$$\ln\left[\frac{1-\phi}{\phi}\right] = \ln\left[\frac{1-\phi_0}{\phi_0}\right] - k_s t$$

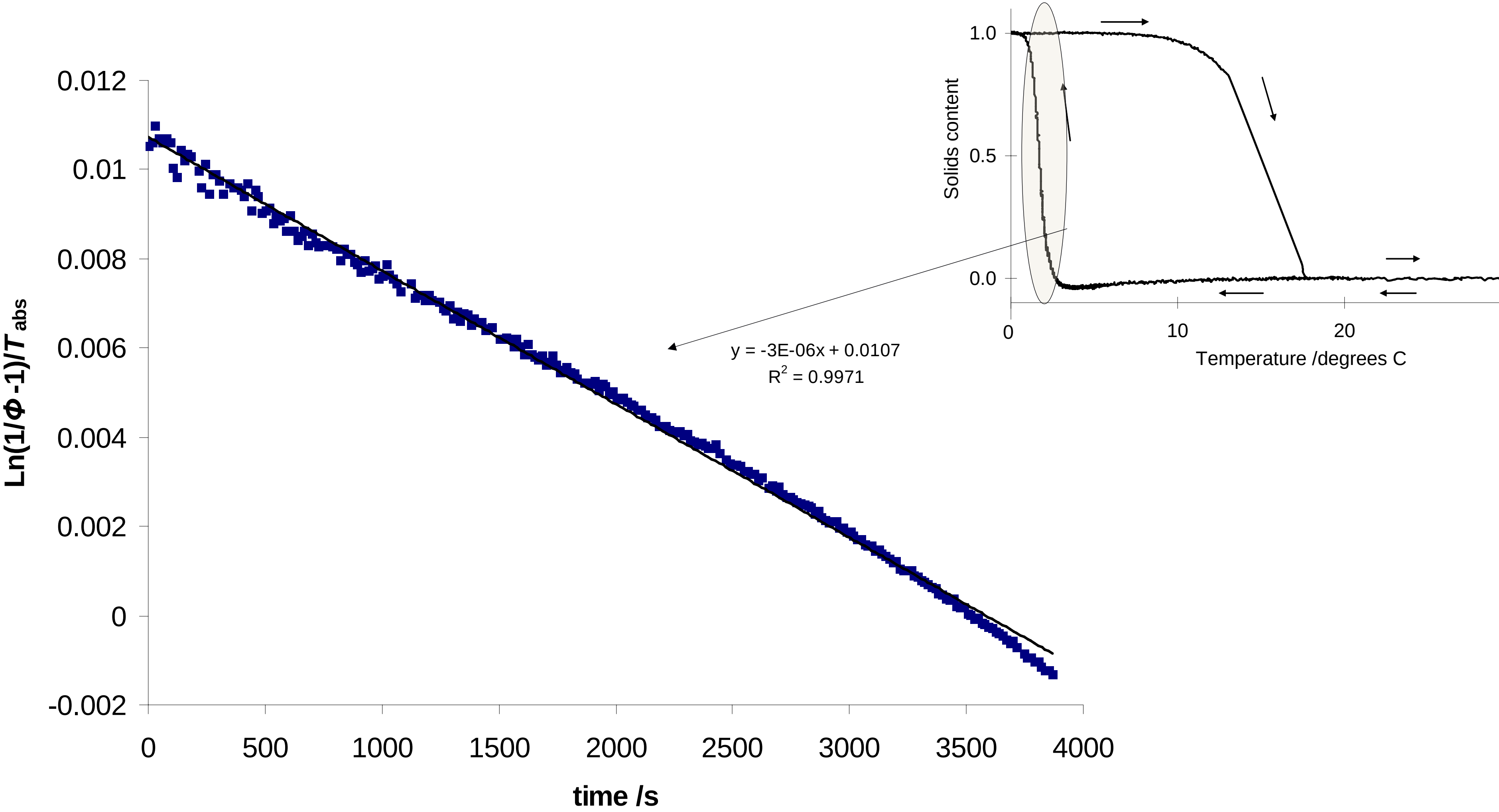
Potential barrier to collision nucleation

$$= \qquad k_B T \ln(w)$$

where the collision rate

$$w = \frac{k_S 3\eta}{8 k_B T n_0}$$

Determine the kinetics



Collision mediated nucleation

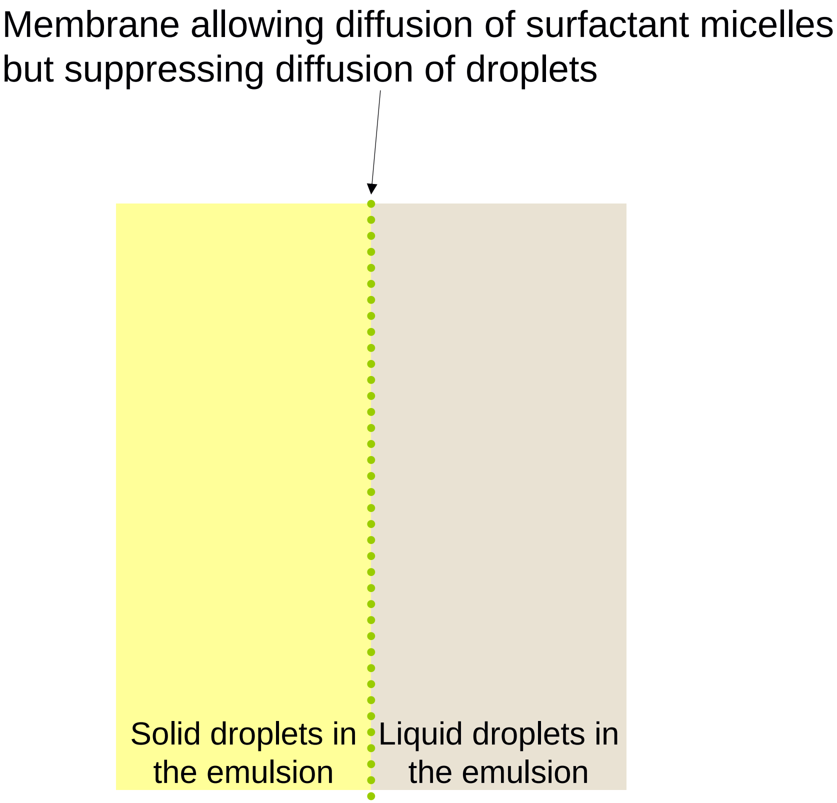
UNIVERSITY OF LEEDS

1. Separate the two emulsions using a semi-permeable membrane.

2. Then remove the membrane to allow mixing.

3. The solid content remains constant until the membrane is removed.

4. The the solid content begins to rise.

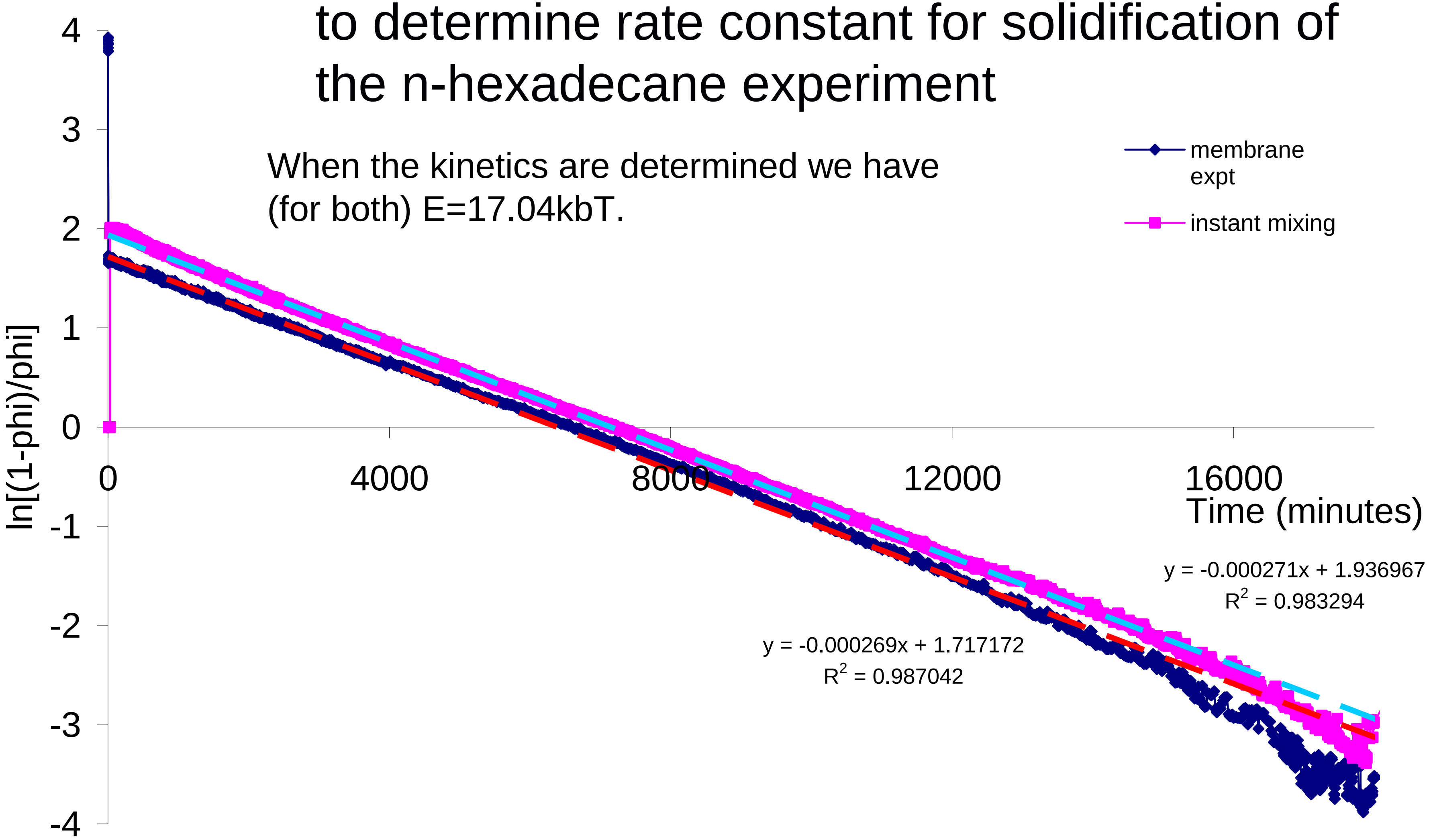


Membrane allowing diffusion of surfactant micelles but suppressing diffusion of droplets

Plot of ln((1-phi)/phi) against time

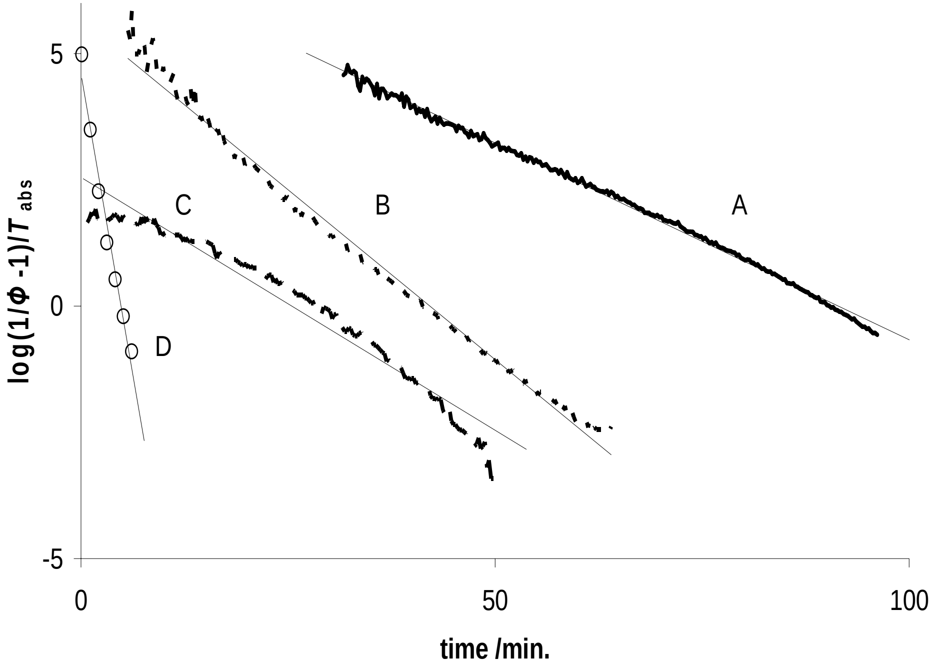
to determine rate constant for solidification of the n-hexadecane experiment

When the kinetics are determined we have (for both) E=17.04kbT.



Crystallization kinetics
n-hexadecane emulsions

A cheesy thought -



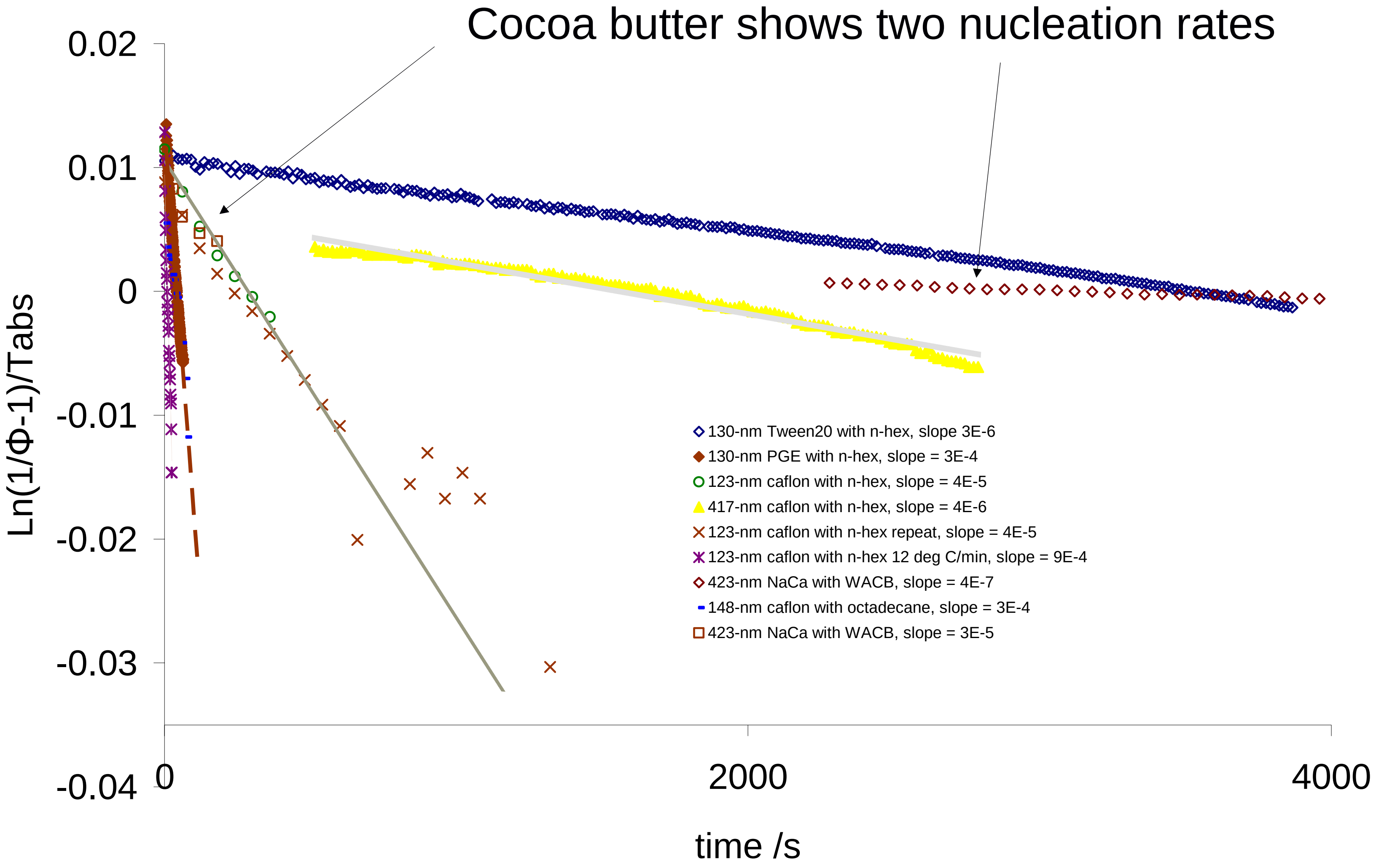
How does our data fit in with classical nucleation theory?

For the two Caflon emulsions, presumably identical in all respects apart from size, the slopes whose measured ratio is 0.1001/0.9544 = 9.544 should have the ratio which if *x*=2 is 7.20 and if *x*=3 is 19.30.

We conclude here that at least in the case of the Caflon stabilised emulsion, nucleation is dominated by surface heterogeneous nucleation.

A: 130-nm Tween20
B: 130-nm L-7D, dotted line
C: 320-nm Caflon, dashed line
D: 130-nm Caflon, open circles

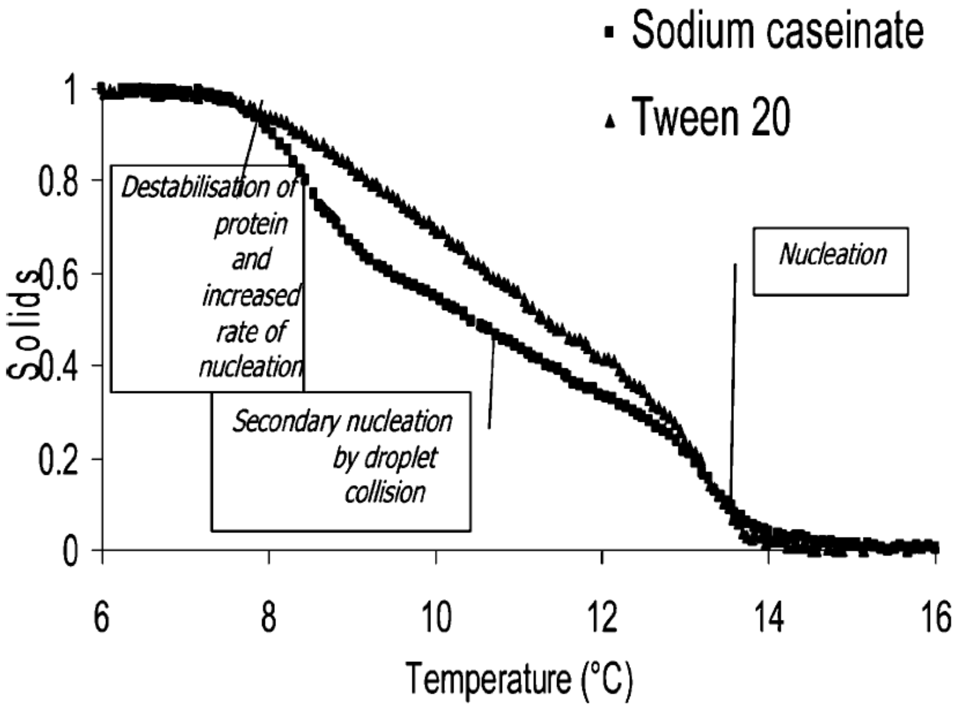
… more detail



Cocoa butter shows two nucleation rates

Cocoa butter emulsions

UNIVERSITY OF LEEDS



Melting Point Depression of the Surface Layer in *n*-Alkane Emulsions and Its Implications for Fat Destabilization in Ice Cream

Malcolm J. W. Povey,*[†] Scott A. Hindle,[†] Asbjorn Aarflot,[‡] and Harald Hoiland[‡]

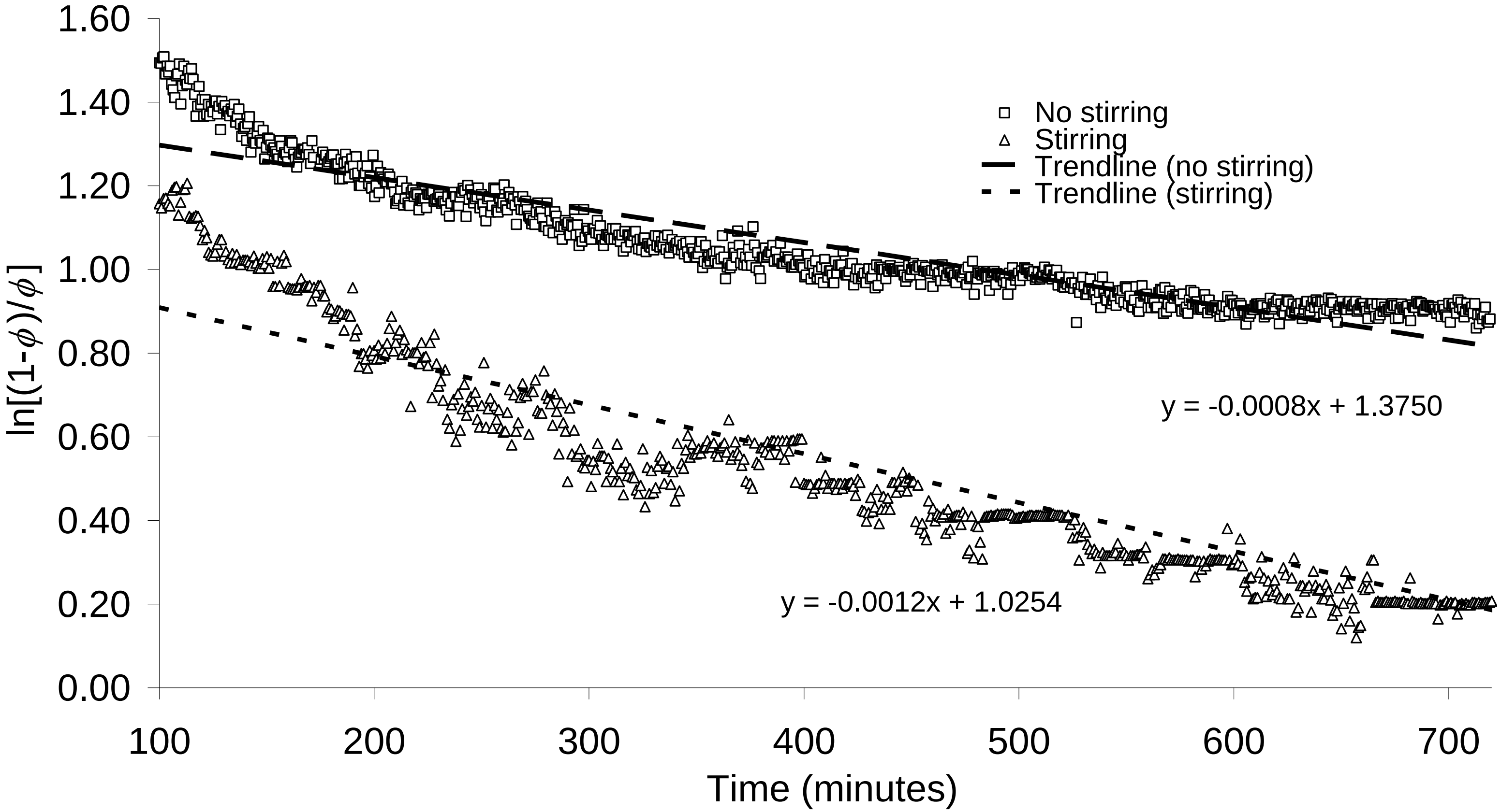
Department of Food Science, University of Leeds, Leeds, LS2 9JT, U.K., and University of Bergen, N-5020 Bergen, Norway

CRYSTAL
GROWTH
& DESIGN

2006
VOL. 6, NO. 1
297−301

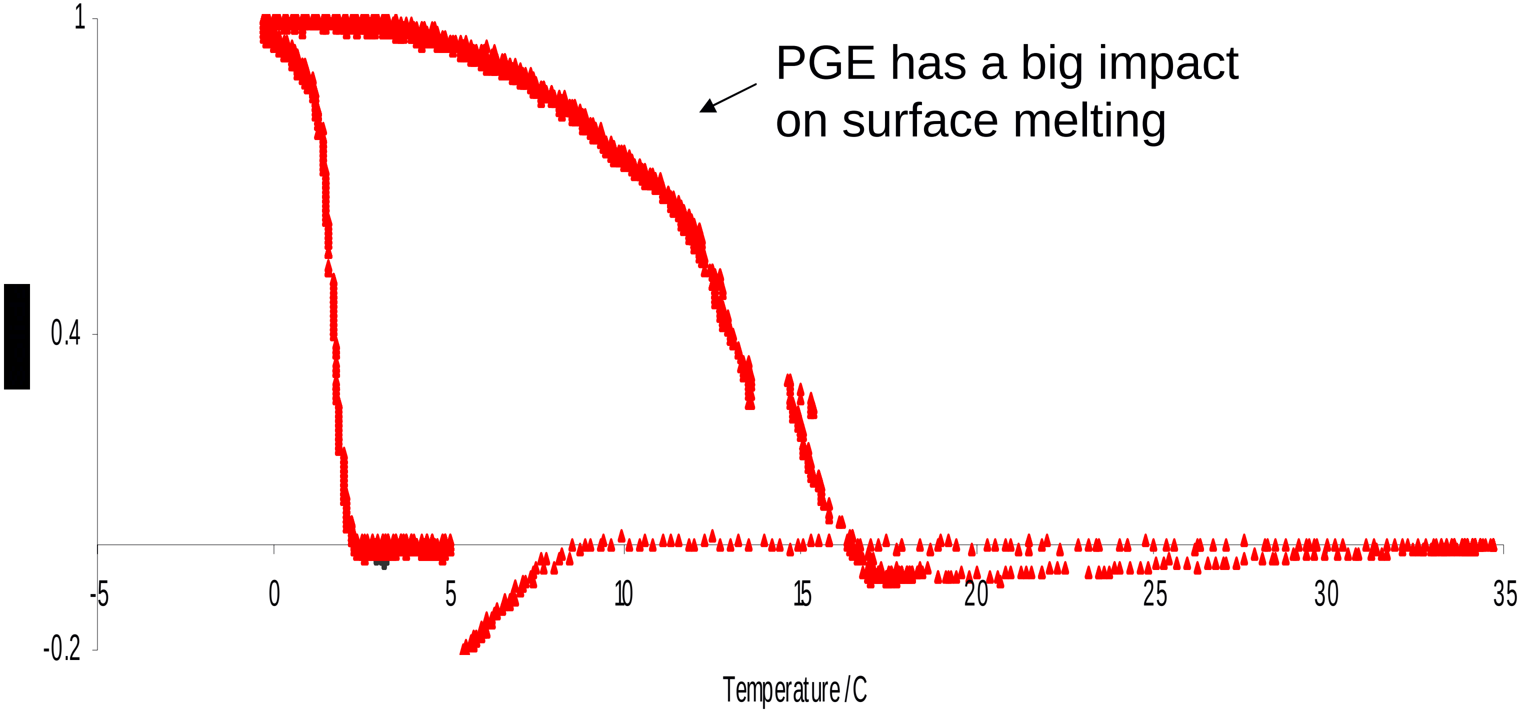
Effect of stirring

UNIVERSITY OF LEEDS

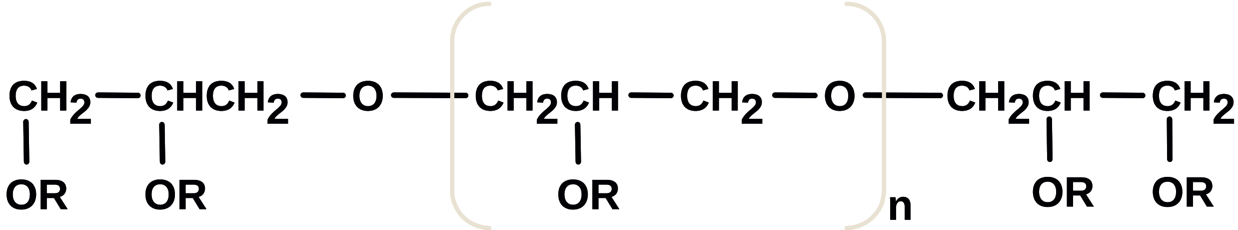


Melting point depression and surfactant dissolution

UNIVERSITY OF LEEDS



PGE has a big impact on surface melting



$$\underset{OR}{CH_2}-\underset{OR}{CH}CH_2-O-\left[\underset{OR}{CH_2CH}-CH_2-O\right]_n-\underset{OR}{CH_2CH}-\underset{OR}{CH_2}$$

n=10 and R=lauric acid

Factors influencing nucleation in emulsions containing nano-particles

UNIVERSITY OF LEEDS

Diffusion rate,

collision rate,

surfactant stabilising barrier energy,

surface energy,

surface displacement

van der Waals forces

Steric (inter surfactant) forces

Particle size distribution and particle size

Surfactant ‘micelle’ diffusion rate and surface attachment energy.

Summary of kinetic data

Oil	Surfactant	Particle size D[3,2] (nm)	Crystallization Temperature/ undercooling (ºC) ‡	$k_x/T \times 10^6$ (K^{-1} s^{-1})	n_c *The number of collisions per second per unit volume*	*1/w The fraction of collisions leading to nucleation* $\times 10^6$	*E= k.T.ln(W) Energy barrier to nucleation*
n-hexadecane	Tween 20	2440	1.5/16.7	^^			
		800[13]	2.5/14.7				
		360[13]	3.5/13.7	7.4	7	0.99	13.8
		160	2.9/14.3				
		130	3.1/14.1	3	252	3.3	12.6
	Caflon phc060	417	3/14.2	4	8	144	8.8
		330	2.8/14.4				
		139	1/16.2				
		123	1.1/16.1	40	75	148	8.8
		123‡	1.4/15.8	900	74	334	5.7
		123[7]	3.1/14.1				
		50**	9.6/8.6**				
	PGE	130[7]	2.3/14.9	3	63	1310	6.64
n-octadecane	Caflon phc060	148	11/18.5	200	44	1940	6.25
	Tween 20	3450[9]	13/16.5				
		450[9]	12.5/17				
		150[9]	12/17.5				
	Sodium caseinate	3450[9]	14/15.5				
		450[9]	13.5/16				
Cocoa butter	Tween 20[10]	2400	14.2/18	100	1093	0.09	16.2
	Sodium caseinate[10]	2400	14.2/18	0.4	8	15	11.1
				30	8	1130	6.8

** is data from a microemulsion.

† These data are consistent with dissolution of the surfactant (PGE) into the bulk of the oil.

‡ Crystallization temperature is defined as the temperature at which the solids constant is noted to rise above zero, at a given cooling rate. The cooling rate is 1 oC/min in all experiments apart from the cocoa butter, in which case the experiments were carried out isothermally and the 123-nm Caflon stabilised emulsion, which was cycled first at 1 ºC/min then at 12 ºC/min.

^^ The nucleation in this sample occurred too quickly to measure.

Conclusion

As particle size reduces, so the role of surfactant in crystal nucleation of the emulsion dispersed phase changes and influences nucleation and growth, through the process of droplet collision mediated nucleation, whilst surface heterogeneous nucleation through templating appears to have less importance

Classical nucleation theory, modified, has a role to play once collision and stirring are taken into account.

Thank you for your attention.

Lots more to see at www.food.leeds.ac.uk/mp.htm