Modelling the phase and crystallisation behaviour of fat mixtures

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- Introduction
- Equilibrium
- Kinetics
- The full works

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Collaboration

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Thermodynamics & kinetics

Temperature vs. composition

Equilibrium

Temperature $T_1$

Kinetics

Temperature $T_2$

Equilibrium description not good enough

Composition gradient in solid
Goal

- ‘Complete’ description of crystallisation behaviour of (fat) mixtures
  - segregation
    - undercooling
  - mass transport
  - heat transport
  - nucleation
  - polymorphism (including metastable phases)
- Kinetics **very** important
- Ambitious…
What is needed?

- Equilibrium phase diagrams
  - often not available
- Kinetic parameters: kinetic phase diagrams
  - often not available
- Algorithm to deal with mixtures
  - MMCG ("Modelling Mixed Crystal Growth") package
Equilibrium binary phase diagrams

- Requires set of thermodynamic parameters
- Ideal mixture of fraction $x$ of B in $(1-x)$ of A

$$G(T, x) = (1-x)G_A(T) + xG_B(T) + RT[(1-x)\ln x + x\ln x]$$

- parameters of pure compounds are sufficient
- Deviations from ideal: excess functions

$$G(T, x) = (1-x)G_A(T) + xG_B(T) + RT[(1-x)\ln x + x\ln x] + G^E(T, x)$$

- excess enthalpy (heat of mixing): $H^E$
- excess entropy: $S^E$
- e.g., regular solution: $H^E \neq 0; \quad S^E = 0$
- expressions of different sophistication possible for excess functions, e.g. a Redlich-Kister expansion

$$G^E(T, x) = A x(1-x) \{1 + B(1-2x) + C(1-2x)^2 + ... \}$$
Equilibrium phase diagrams

- To do: determine thermodynamic parameters
- However: complicated by kinetics
  - less segregation than predicted from equilibrium
  - solid composition closer to liquid composition
  - happens in reality
Low supersaturation

- Assumptions
  - no diffusion in solid
  - homogeneous liquid
  - crystallizing solid locally in equilibrium with liquid
- Then: concentration gradient in solid
Determination of phase diagram

- Cooling path
- Temperature increase
- Nucleation
- Near equilibrium
- Far from equilibrium

Enthalpy

- Experiment
- Kinetic model
- Equilibrium model
Determination of phase diagram

- Kinetic model
  - derive excess enthalpy and entropy
  - fast way to find equilibrium phase diagram

Matovic et al., Calphad 30 (2006) 209.
Kinetic phase diagrams

• System typically does not follow equilibrium phase diagram: include kinetics

• Linear kinetic segregation model (LKS)
  • flux of component $i$ to solid ($J^+$) and from solid ($J^-$) are related by
    \[
    \frac{J_i^+}{J_i^-} = \exp\left(\frac{\Delta \mu_i}{RT}\right)
    \]
  • growth rate of component $i$ 
    \[ R_i = K_i \sigma_i \]
  • yields net flux, dependent on supersaturation
  • (yields thermodynamic equilibrium for zero growth)
Examples

- less segregation due to kinetics
- larger effect for larger supersaturation


P = palmitic acid
S = stearic acid
O = oleic acid
My = myristic acid
Other kinetic models

- Monte Carlo simulation of binary Kossel model
  - few assumptions
- Mean field kink site kinetic segregation model (MFKKS)
  - moderate/large undercooling
- Combination of LKS with MFKKS yields best results
- LKS still good starting point
Kinetic phase separation domains

- Near eutectic point
  - simultaneous growth of solid phases with different (and non-equilibrium) composition

Los et al., Calphad 30 (2006) 216.
Combining everything (MMCG)

1. Equilibrium phase diagrams
2. Kinetic phase diagrams
3. Multi-component systems (equilibrium + kinetics)
   • parameters for every relevant phase/component
4. Time & temperature evolution
   • growth
   • melting
   • nucleation
   • polymorphic transitions

NEW!
Differential scanning calorimetry (DSC)

- binary fat mixture
  - EEE & SSS ($x_{SSS} = 0.32$)
    - E = elaidic acid
    - S = stearic acid

experiment

modelling for different cooling rates

- $0.2 \, ^\circ\text{C}/\text{min}$
DSC - effect of kinetic constants

growth velocity constant

nucleation constant
Fat blend with 32 components

• Cool/isothermal/heating sequence 350 → 285 → 350°C

Several β polymorphs

Sequence α → β' → β
Summary

- DSC
- polymorphic transitions
- melting

- equilibrium binary phase diagrams
- pure & excess parameters
- kinetic binary phase diagrams
- kinetic parameters
- multi component phase diagrams (polymorphs)
- from binary data
- crystallisation process
- nucleation, time/temperature profile

feedback
Conclusions and outlook

• Kinetics are crucial during crystallisation
  • crystallisation = kinetics
• Thermodynamic + kinetic parameters + models → ‘full’ description of crystallisation of mixtures
• Software available

• Derive efficient approximation for excess functions for wide range of fats
  • make use of modelling capabilities
  • make use of Monte Carlo simulations