Eutectic freezing
one concept, different applications

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Outline

1. Eutectic freezing
2. Application in water treatment
3. Osmotic virial equation (OVE)
4. Objectives of my research
Eutectic point on phase diagram
binary system

NaCl – water phase diagram

http://people.ucalgary.ca/~kmuldrew/cryo_course/cryo_chap6_1.html
**Phase diagram of ternary system**

![Phase diagram of ternary system](http://faculty.uml.edu/nelson_eby/89.304/IMAGES/Ternary%20projections.jpg)

**Eutectic freeze crystallization (EFC)**

EFC is a technique for separating water and solutes based on the existence of a eutectic point, where an equilibrium exists between ice, salt and a solution with a specific concentration. Below the Eutectic temperature no liquid phase can exist.

**Benefits of EFC [1]**

- High purity of water, with no additional chemicals
- Extraction of valuable salt from waste water
- Lower energy consumption compared to evaporation techniques
  - Enthalpy of evaporation is ~7 times higher than enthalpy of freezing
  - The ice that is formed can be used for pre cooling

Goal: Use osmotic virial equation of state (OVE) to predict eutectic point

Multi-component solution behaviour can be predicted from single-component OVE coefficients (that are obtained from fitting to experimental data).

This method has been used to predict the ice freezing point as a function of solution concentration - the ice liquidus (region 1).


Use of the OVE in the ice precipitating region

For binary system:
\[ \pi = m_i + B_i m_i^2 + C_i m_i^3 + \cdots \]

Me₂SO \((i=2)\), Glycerol \((i=3)\)

R = mass glycerol/mass Me₂SO

\[ \pi = m_2 + m_3 + B_2 m_2^2 + B_3 m_3^2 \\
+ (B_2 + B_3) m_2 m_3 + C_2 m_2^3 + C_3 m_3^3 \\
+ 3(C_2 C_3)^{1/3} m_2^2 m_3 \\
+ 3(C_2 C_3)^{1/3} m_2 m_3^2 \]

Prickett et. al., Application of the osmotic virial equation in cryobiology, Cryobiology 60, 2010
Why OVE?

1. In its single-solute form, the OVE is applicable to a wide range of solutes including: macromolecules, electrolytes, inorganic and organic components.

2. Prediction of multi-component solution does not require fitting to multi-component solution experimental data.

<table>
<thead>
<tr>
<th>Binary solution</th>
<th>( \pi = m_2 + B_2 m_2^2 + C_2 m_2^3 + \ldots )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multi-component solution</td>
<td>( \pi = \sum_{i} \sum_{j} \frac{(B_i + B_j)}{2} m_i m_j + \sum_{i} \sum_{j} \sum_{k} (C_i C_j C_k)^{1/3} m_i m_j m_k )</td>
</tr>
</tbody>
</table>


Thank you.
Back up slides

http://www.reciprocalnet.org/edumodules/crystallization/images/crystallization.jpg
Relation between T and $\pi$ ($m_2$)

**Region 1** (solid phase is ice)

- @ equilibrium: $\mu_1^L(T,P,x_2) = \mu_1^S(T,P)$
- $\mu_i$ from Gibbs-Duhem

\[
\pi = -\frac{\mu_i - \mu_i^0}{RTM_1} \mu_1^L(T,P,x_2) = \mu_1^L(T,P,x_2) + \bar{v}_1^L(p - P_{ref}) + \bar{S}_1^L(T - T_{ref}) - \bar{v}_1^L \pi
\]

Also

\[
\mu_1^S(T,P) = \mu_1^S(T_{ref}, P_{ref}) + \bar{v}_1^S(p - P_{ref}) + \bar{S}_1^S(T - T_{ref})
\]

P = constant

\[
\pi = \frac{T_{FP}^o - T_{FP}}{[W_1/(S_1^{oL} - S_1^{oS})]RT_{FP}}
\]