EURO FOOD'S WATER

Water – Disaccharides interactions in saturated solutions and the crystallization conditions

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SURVEY

INTRODUCTION:

- Scope of paper
- The 3 studied disaccharides

Solution Properties :

- Conformation in Solution: FTIR Spectra
- Solubility in Water
- viscosity of disaccharide solutions
- Metastable zone width

Crystallization of disaccharides in water solution

- Nucleation and Pre-nucleation
- Crystal Growth and viscosity
- Role of water in crystallization

Amorphous Disaccharides

- Concentrated Amorphous solution
- Phase diagram revisited

CONCLUSION

SCOPE

Abundant literature on Disaccharides:

Science Direct (30 years) Maltitol (58)<Trehalose(1726)<Sucrose >10000

- Crystal structure - Phase diagram
- Water Solutions - Molecular Modelling
- Glassy State and Phase relations in aqueous solution

Special topic : Explain Biopreservation – Trehalose anomaly

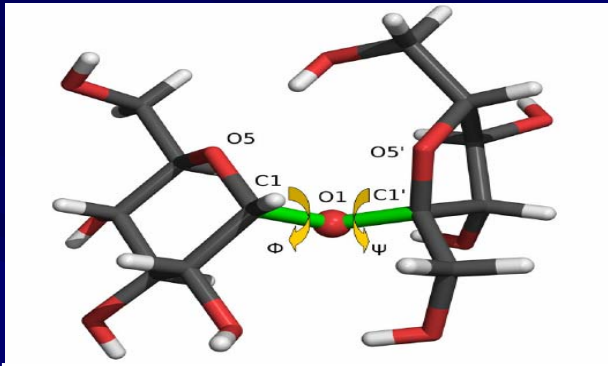
Our Current Work:

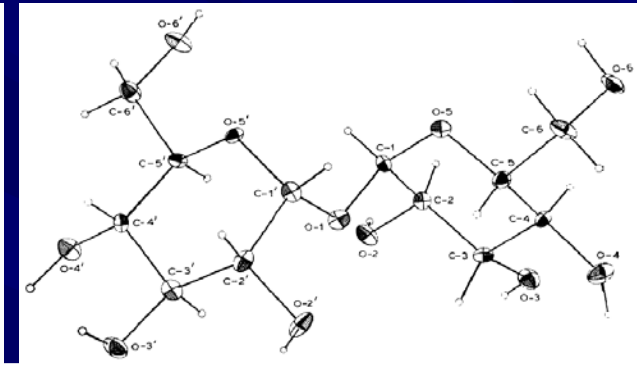
- Understanding molecular association in sugar solutions to optimize their industrial crystallization

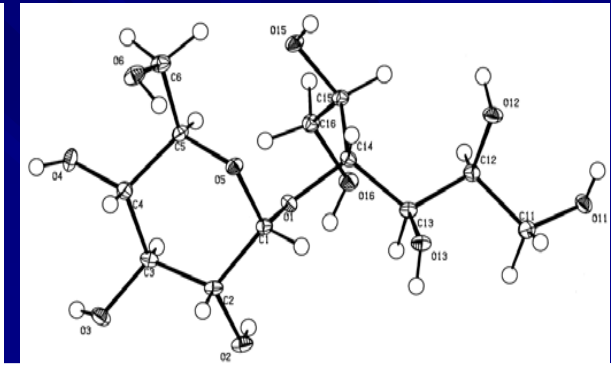
This paper :

- Comparison of solution properties and crystallization conditions for 3 different disaccharides
- Interpretation of behaviour of concentrated amorphous solutions (Glass) based on crystallization

PROPERTIES OF THE 3 DISACCHARIDES

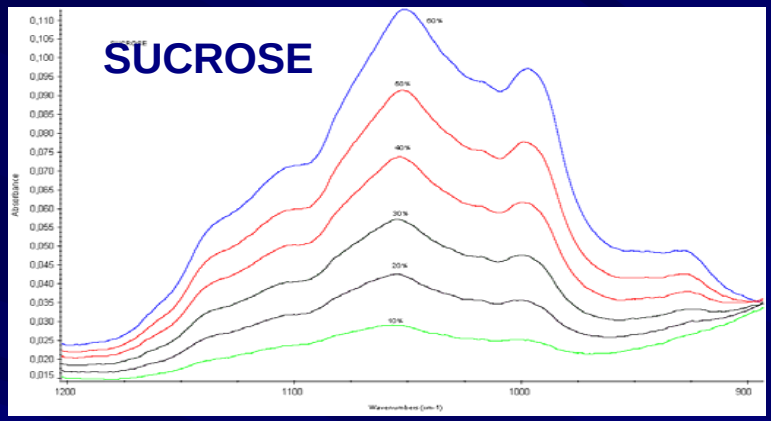


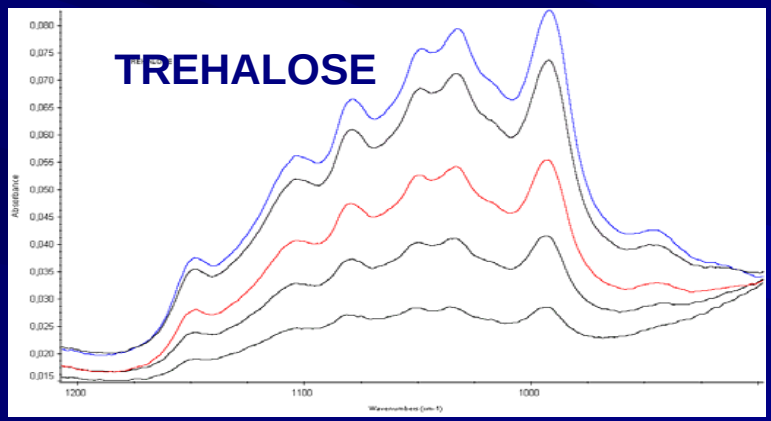


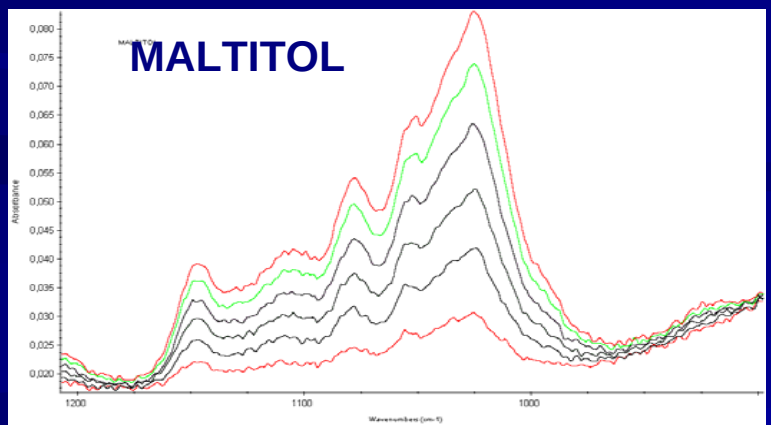


SUCROSE	TREHALOSE	MALTITOL
α-**D**-Glcp *(1→ 2)*β–**D**-Fru*f* ***Anhydrous (m.p. 186°C)***	α-**D**-Glc*p(1→1)*α-**D**- Glc*p* ***Dihydrate* Th *(m.p. 100°C)*** ***Anhydrous Tβ (m.p. 215°C)*** **Unstable Tα; Tγ; Tε; Tκ**	α-**D**-Glc*p(1→4)* glucitol ***Anhydrous (m.p. 146°C)***
Intramolecular H-bonds **Φ = 108.34 ; Ψ = – 44.67°** **Flexibility of Glycosidic linkage**	**No Intramolecular H-bond** **C2 Symmetry** **No Significant difference in structure of Tβ and Th**	**Glucitol moiety folding** **C14-C13 // C16-O16** ***d = 3.09 A° - angle:15.5°***

FTIR SPECTRA OF AQUEOUS SOLUTION







Concentration = 10 – 60%

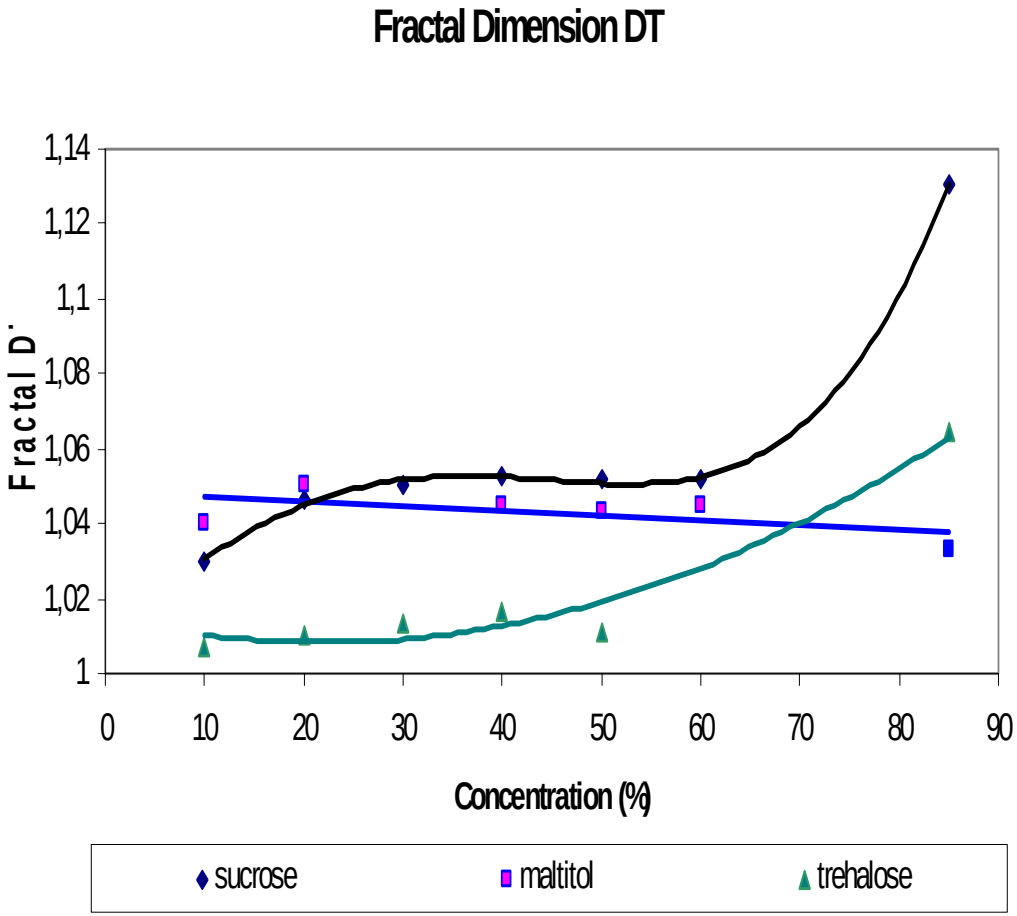
Range explored: 1200 – 900 cm^{-1}
FINGER PRINT REGION

1200 – 1150 cm^{-1}	ν(C – O)
1100 – 1000 cm^{-1}	δ(C-O-H)
1000 – 950 cm^{-1}	δ(C-C-H)
950 – 900 cm^{-1}	ν(C – O -C) g.l.

Differences in FTIR spectra:
- ***Glycosidic bond region***
- ***General shape of bands*** **:**
  assigned to degree of order of disaccharide molecules in solution

FRACTAL DIMENSION OF FTIR SPECTRA

Concentration = 10 – 85%



Fractal Dimension of FTIR spectra is a quantification of the general shape of spectra It informs on the degree of organisation of molecules

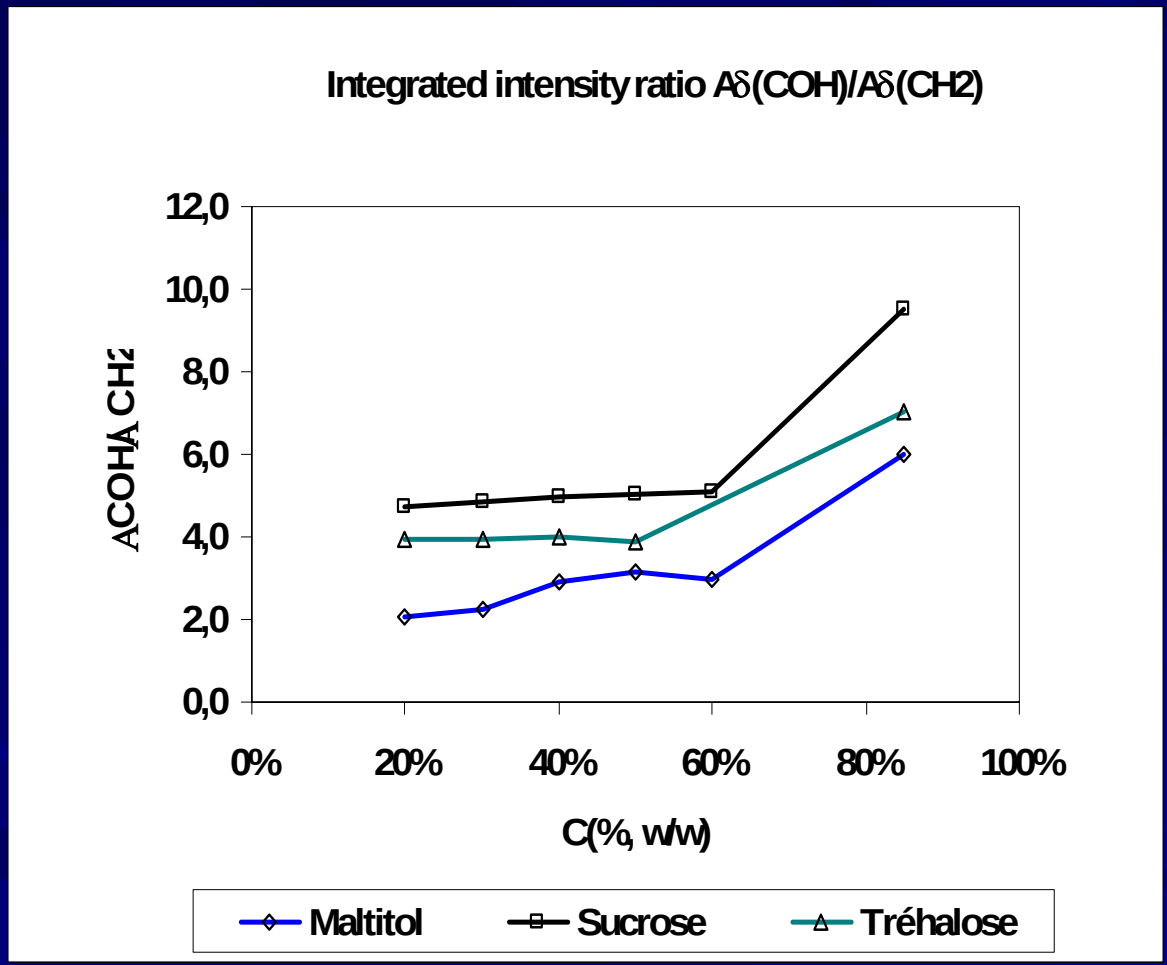
Sucrose Organisation changes around 20 and 60 %

Maltitol Clustering seems independent from concentration

Trehalose Organisation gradually increases with C

FTIR SPECTRA OF AQUEOUS SOLUTION

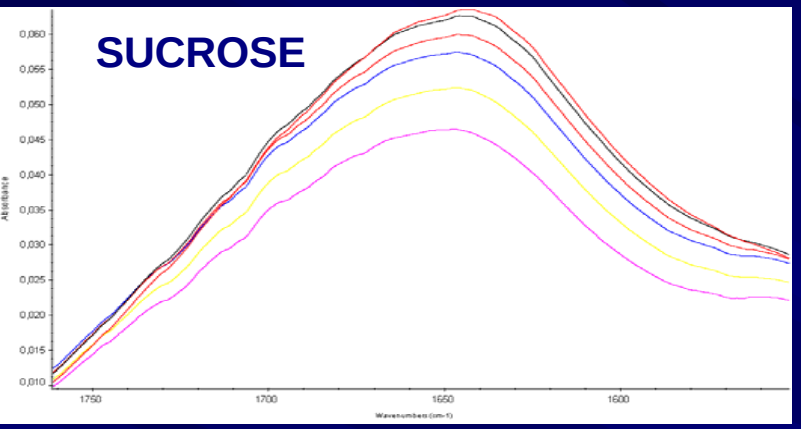
Integrated intensity ratio δ(C-O-H) / δ(H-C-H)

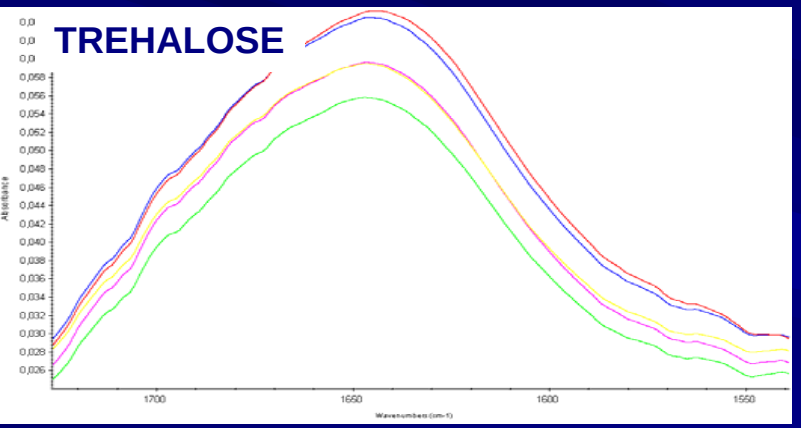


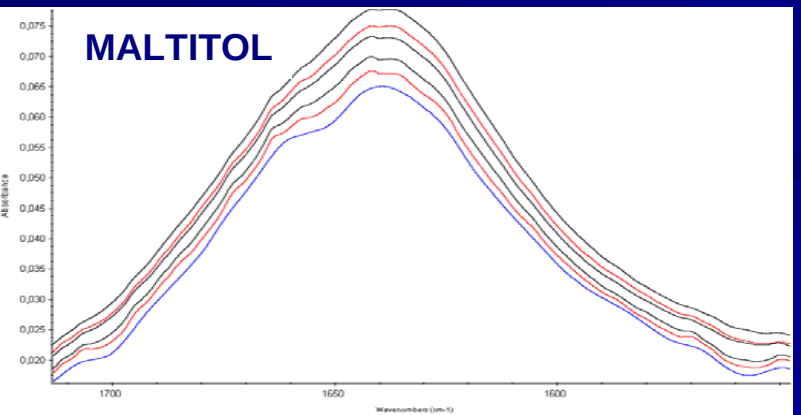
Ratio A δ(COH)/Aδ(HCH): Sensitivity to hydration: Maltitol<Trehalose<Sucrose

Differentiation of dilute and concentrated states: Limit around 60%

FTIR SPECTRA OF AQUEOUS SOLUTION







δ (HOH) i.r. band

SUCROSE: Composite band
- 1640 cm^{-1}: bulk water
- 1674 cm^{-1}: hydration water

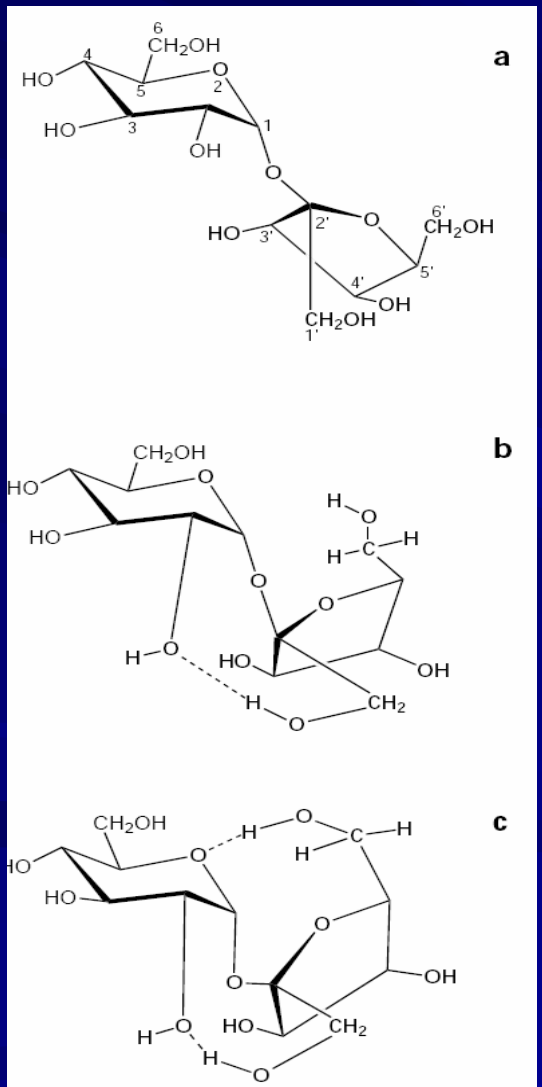
TREHALOSE : Composite band
- 1642 cm-1: bulk water
- 1680 cm-1: hydration water

MALTITOL : Nearly Symmetrical band
- 1640 cm^{-1}: bulk water

CONFORMATION IN AQUEOUS SOLUTION

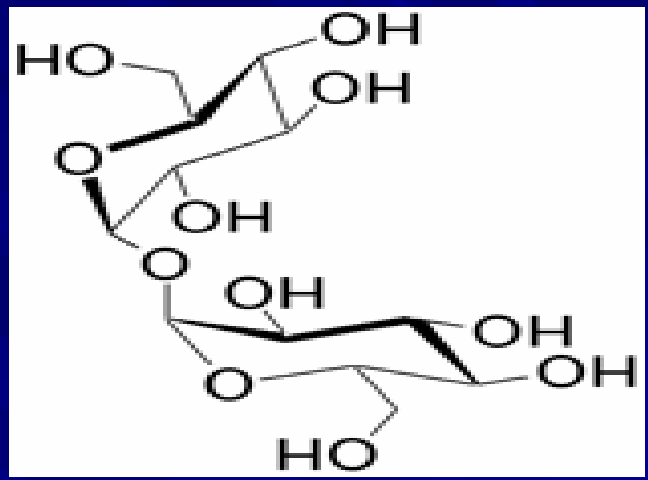
SUCROSE

Flexible



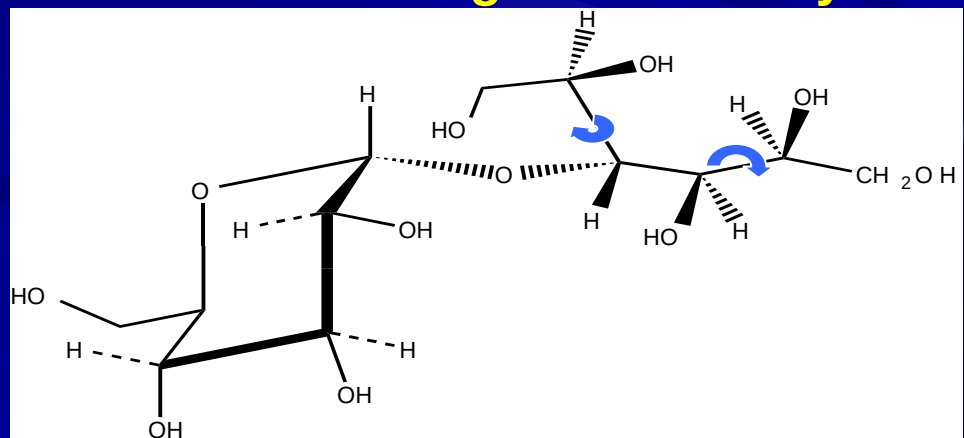
TREHALOSE

Relatively rigid

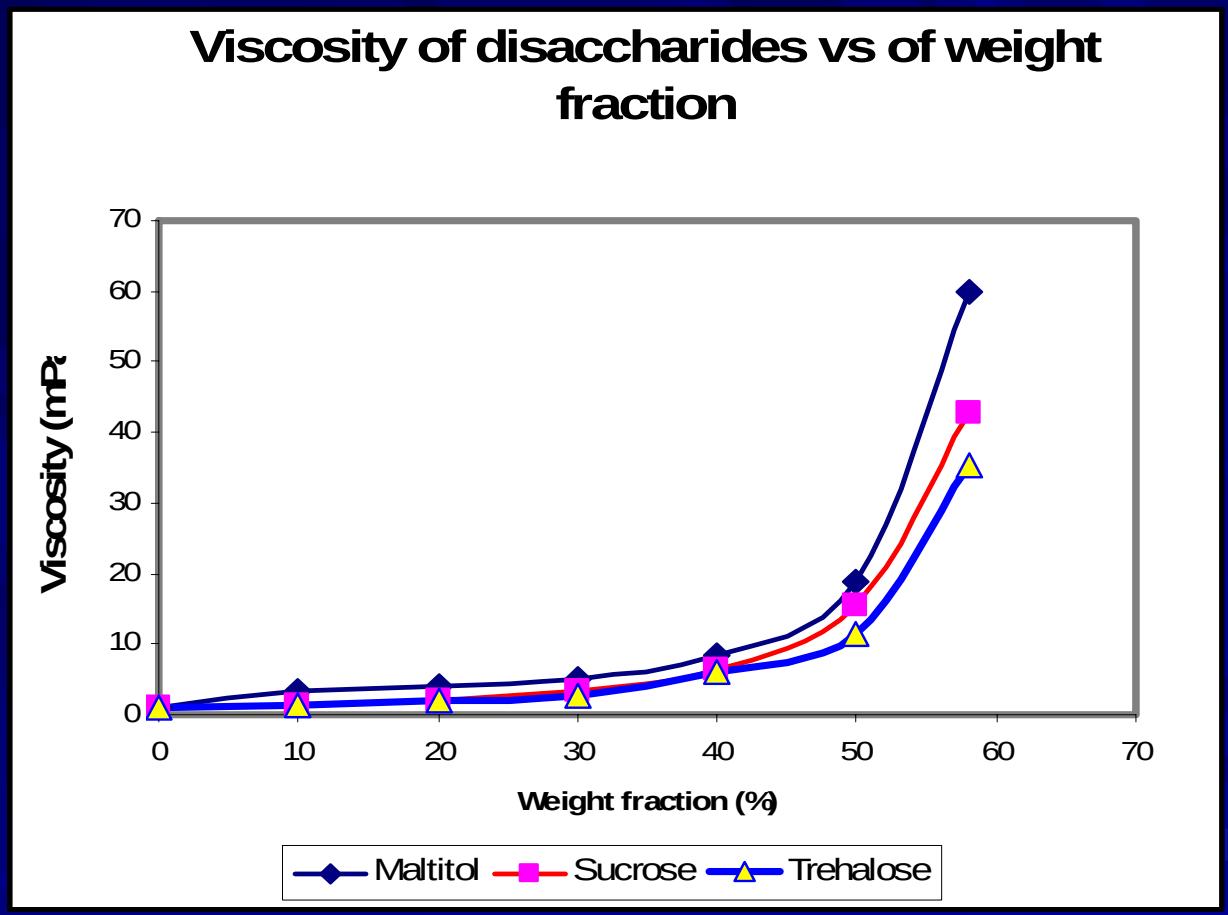


MALTITOL

Motion of the glucitol moiety



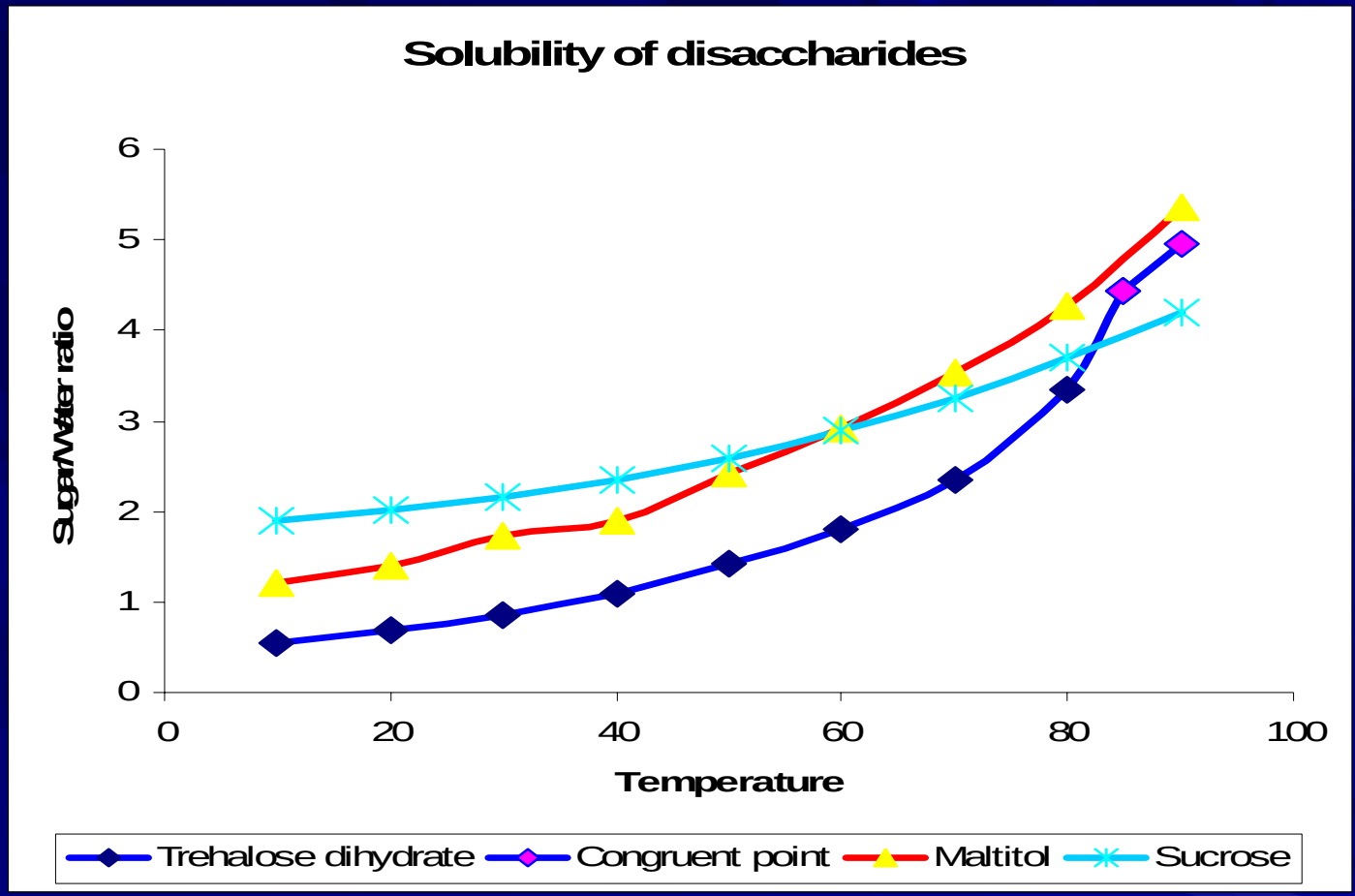
VISCOSITY of AQUEOUS SOLUTIONS



Trehalose < Sucrose < Maltitol

Increase in sugar-sugar association for C > 40%

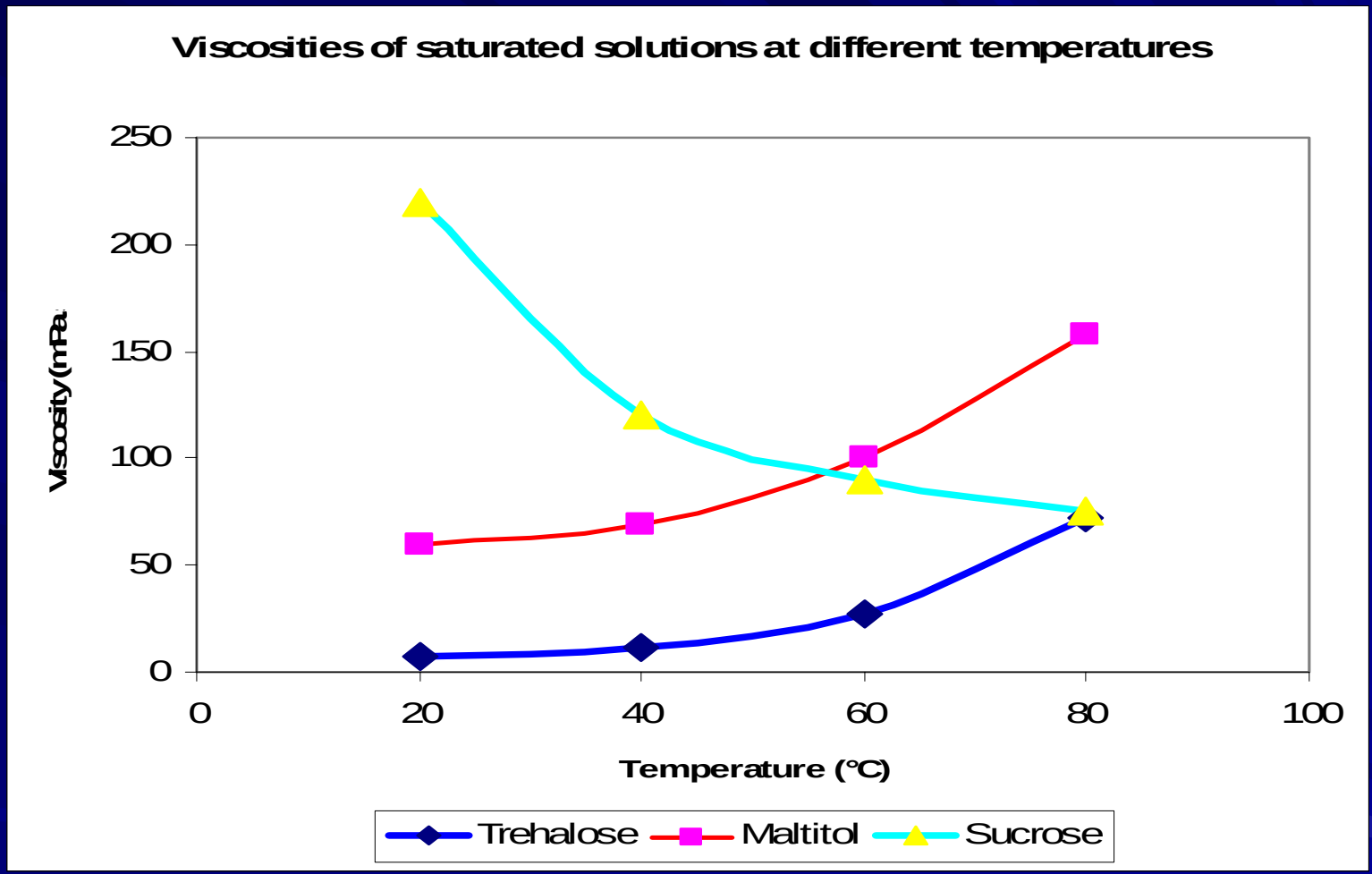
SATURATED SOLUTION PROPERTIES



Solubility Low Temperature: Sucrose > Maltitol > Trehalose

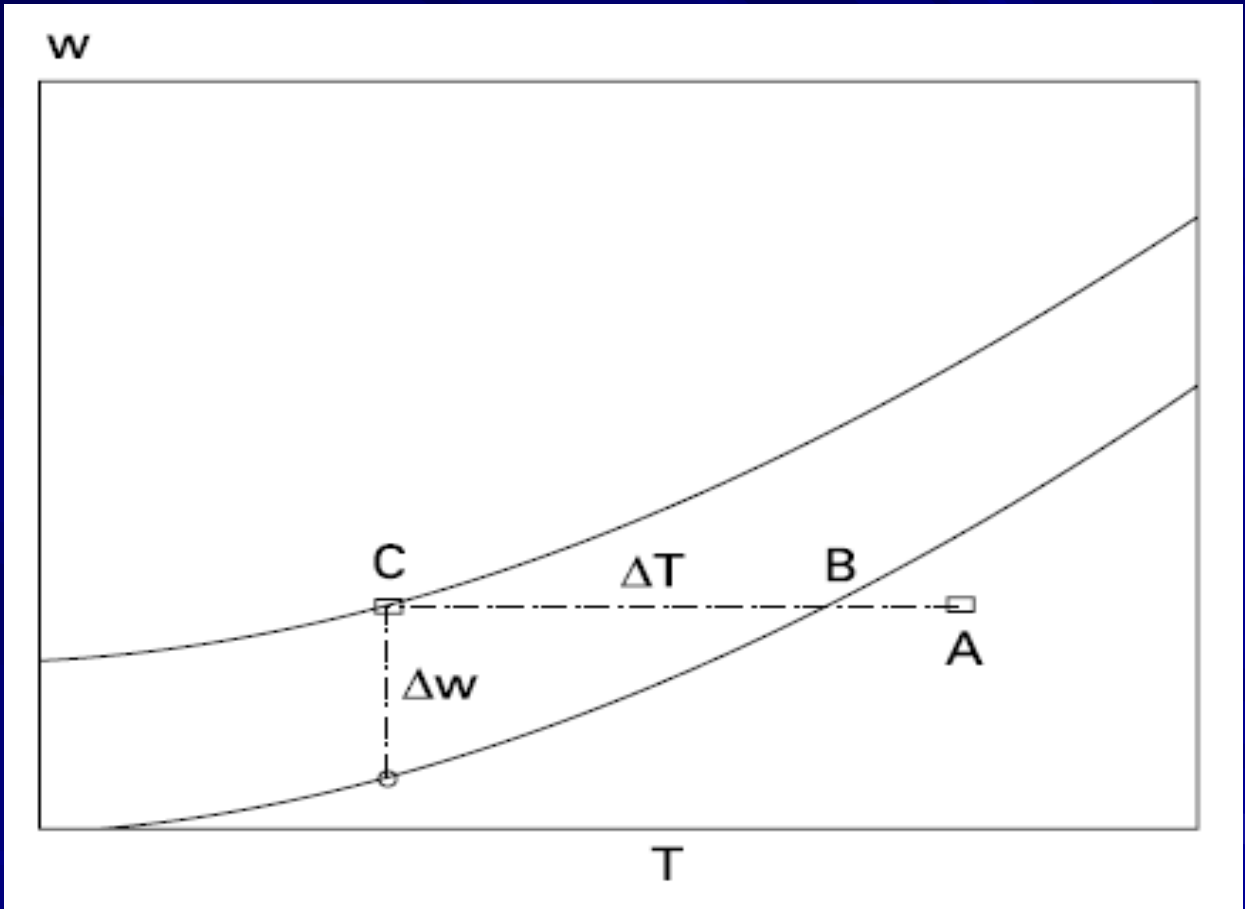
High Temperature : Maltitol > Sucrose > Trehalose (85°C ?)

SATURATED SOLUTION PROPERTIES



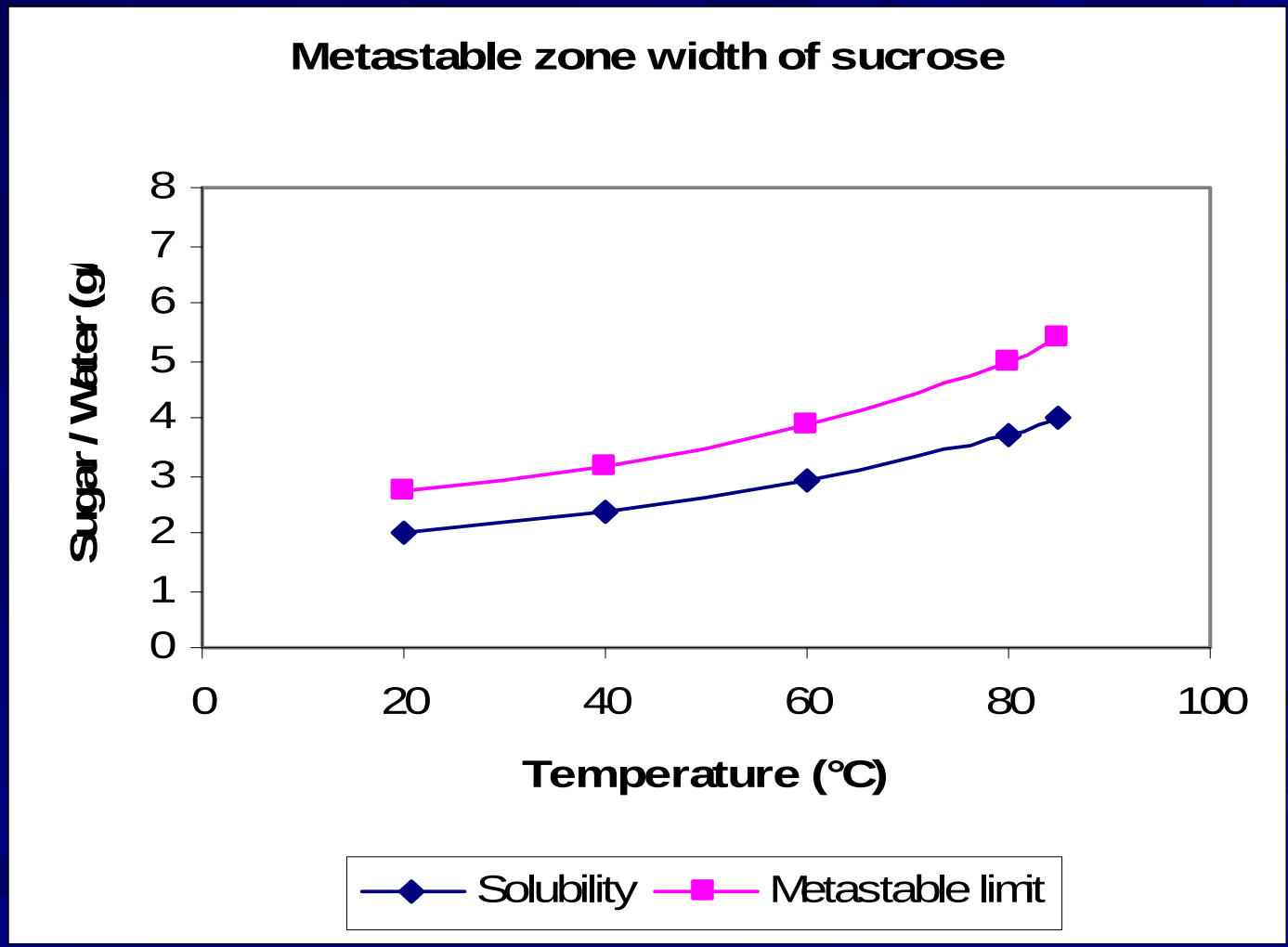
Saturation Viscosity at Low Temperature: Sucrose > Maltitol > Trehalose
High Temperature : Maltitol > Sucrose > Trehalose

METASTABLE ZONE WIDTH DETERMINATION



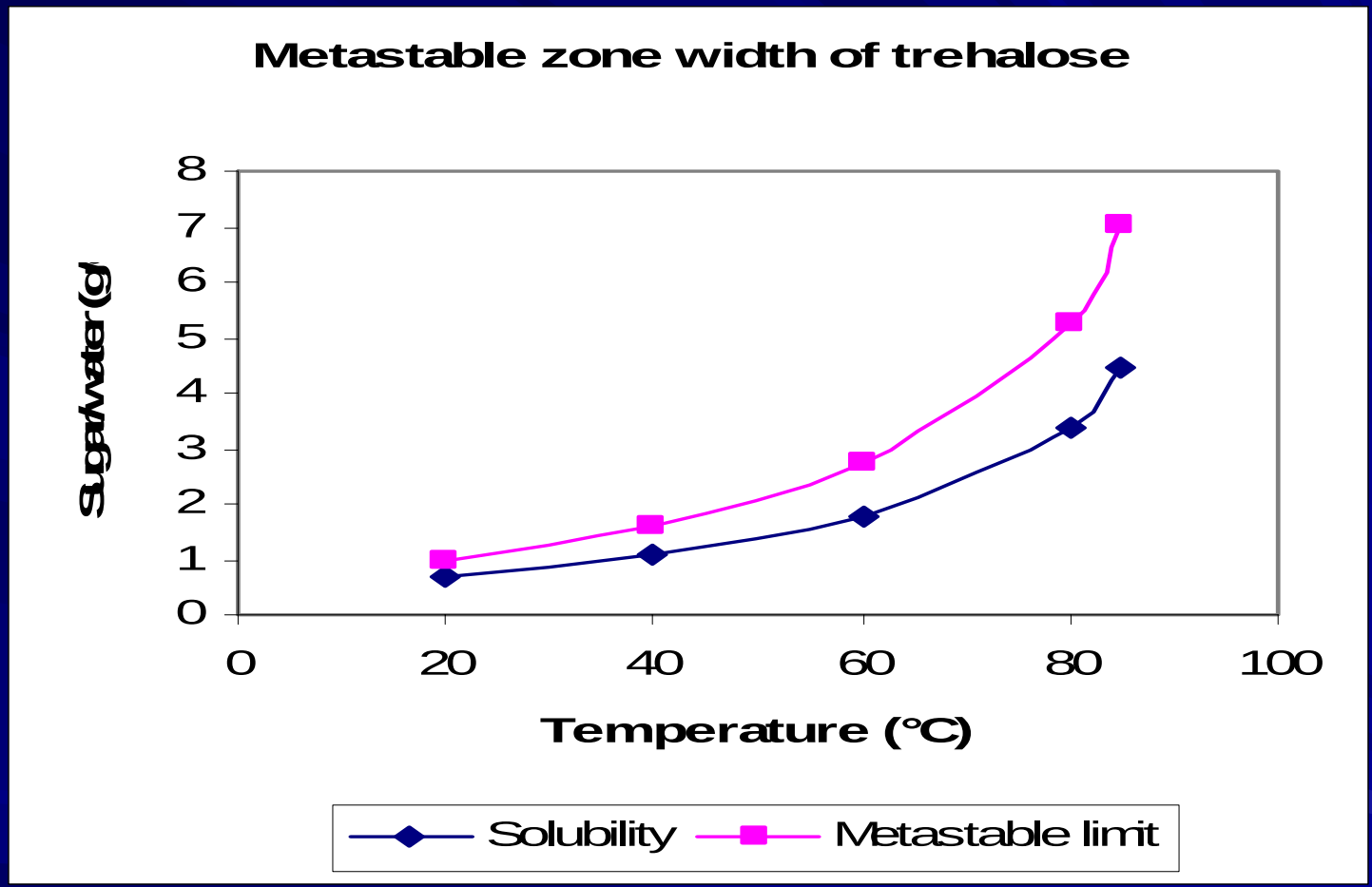
Cooling (ΔT) of undersaturated (A) solution to nucleation (C) limit

METASTABLE ZONE WIDTH



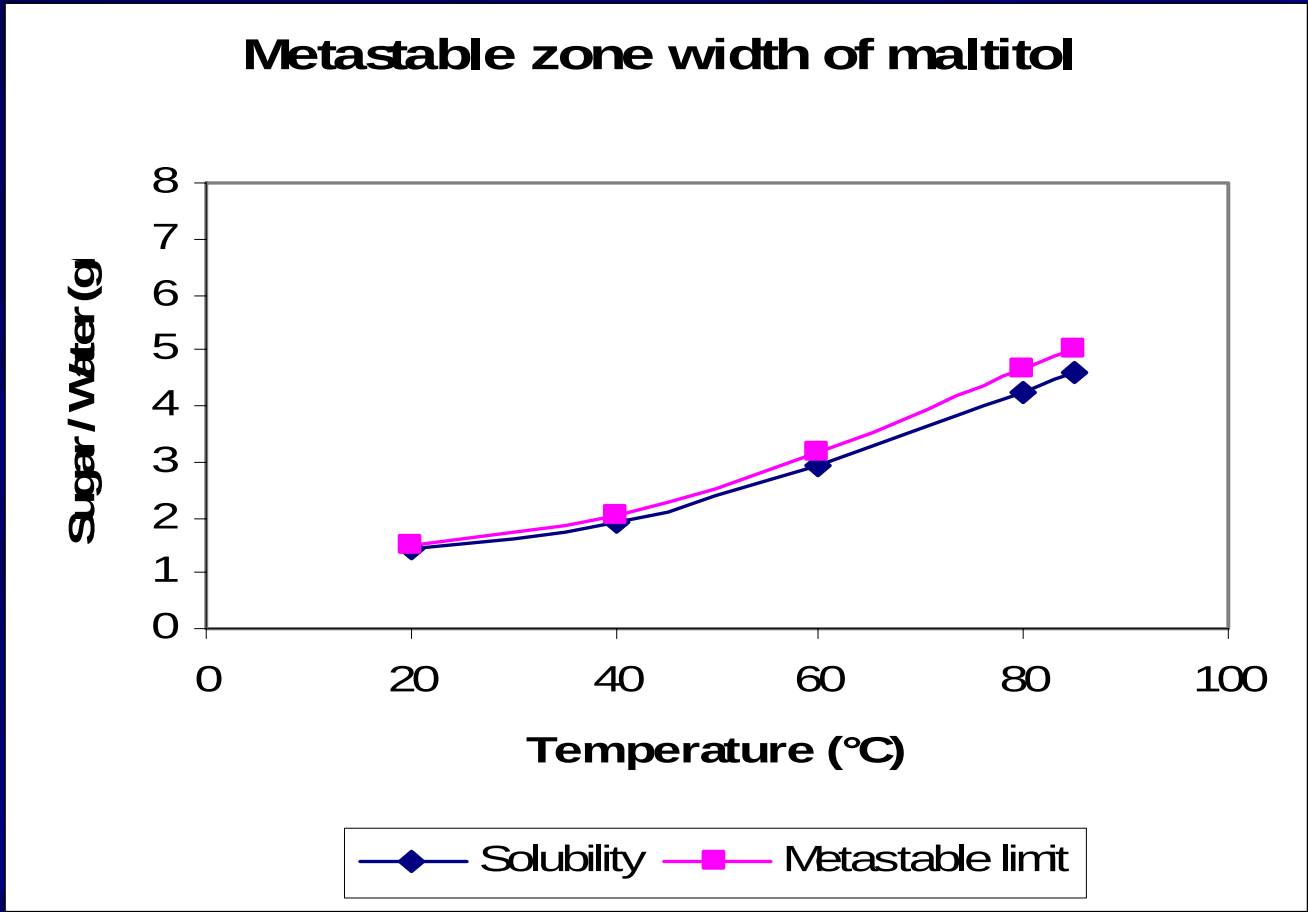
$\Delta \sigma$ = 0.35 in the whole range of temperatures

METASTABLE ZONE WIDTH



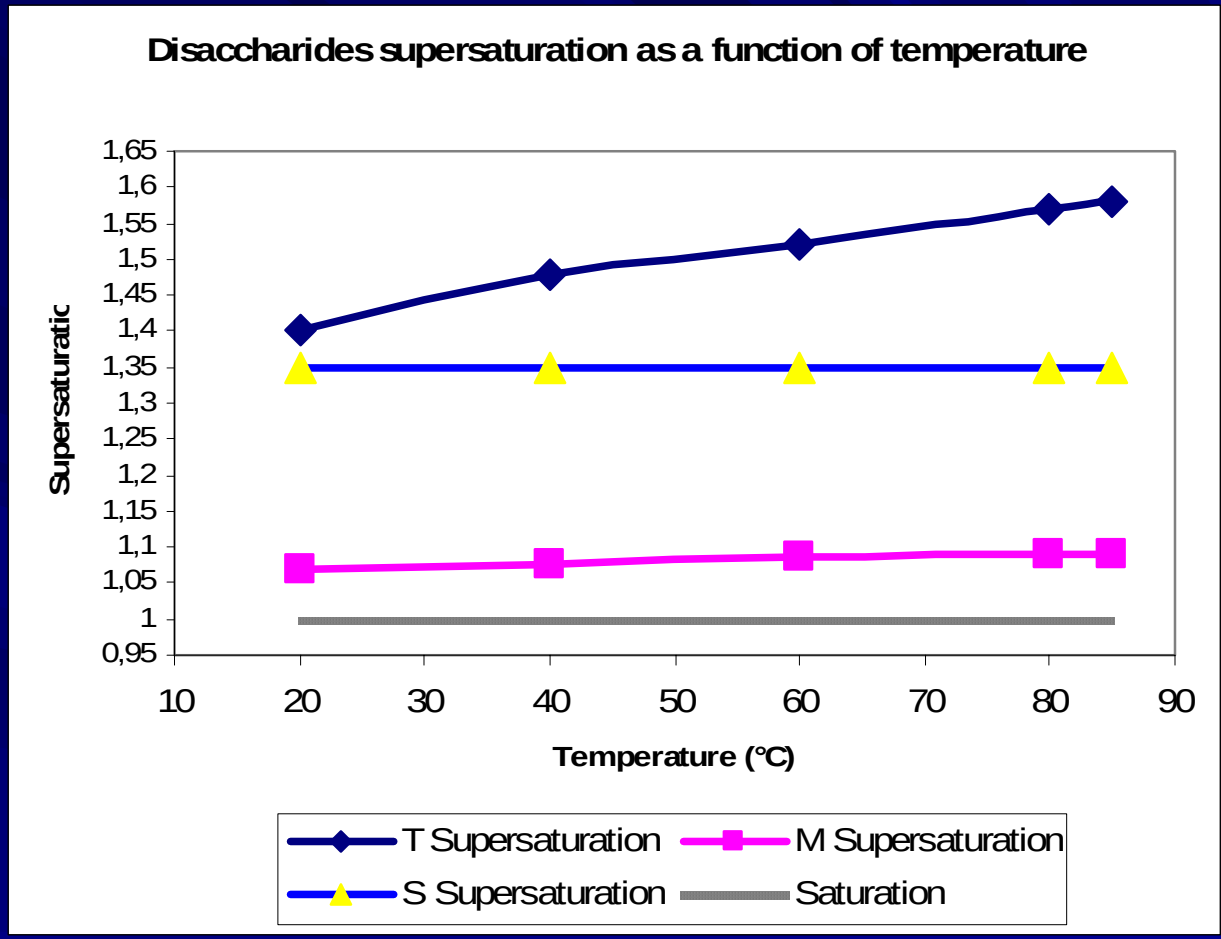
$\Delta\sigma$ = increases from 0.35 to 0.60 with temperature

METASTABLE ZONE WIDTH



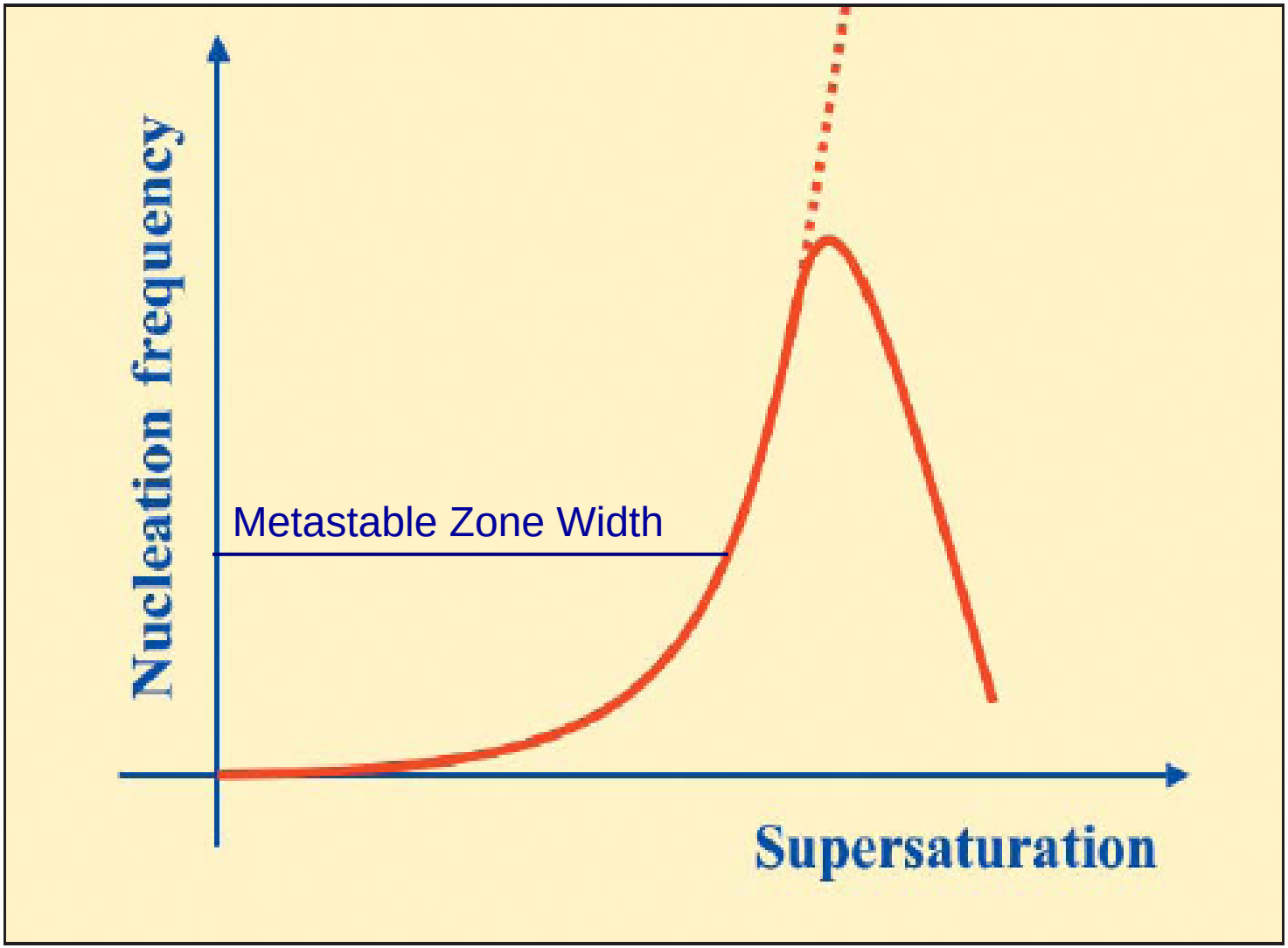
$\Delta\sigma = 0.05$ **to 0.08 between 20 to 85°C**

METASTABLE ZONE WIDTH

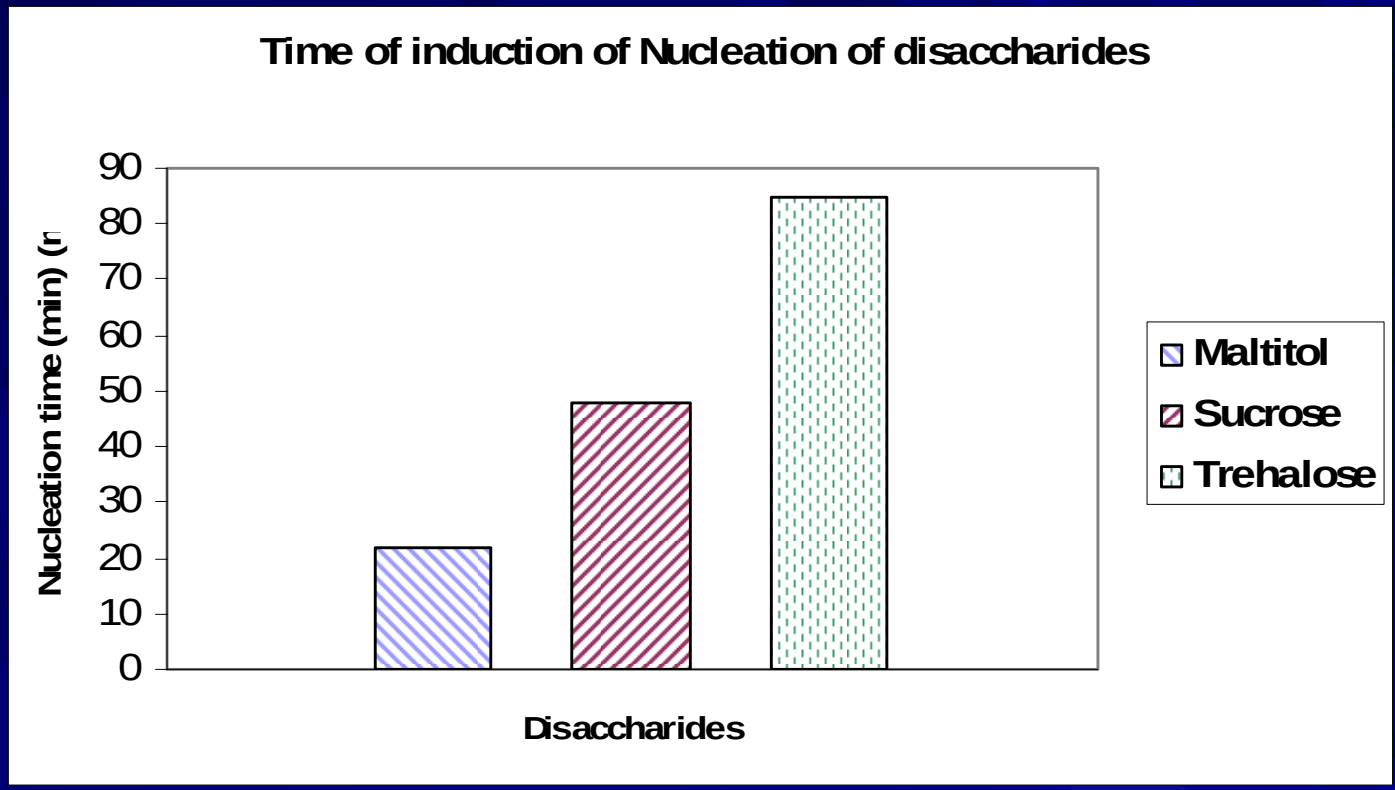


COMPARISON OF 3 DISACCHARIDES METASTABLE ZONE WIDTHS

NUCLEATION


Nucleation frequency
Metastable Zone Width
Supersaturation

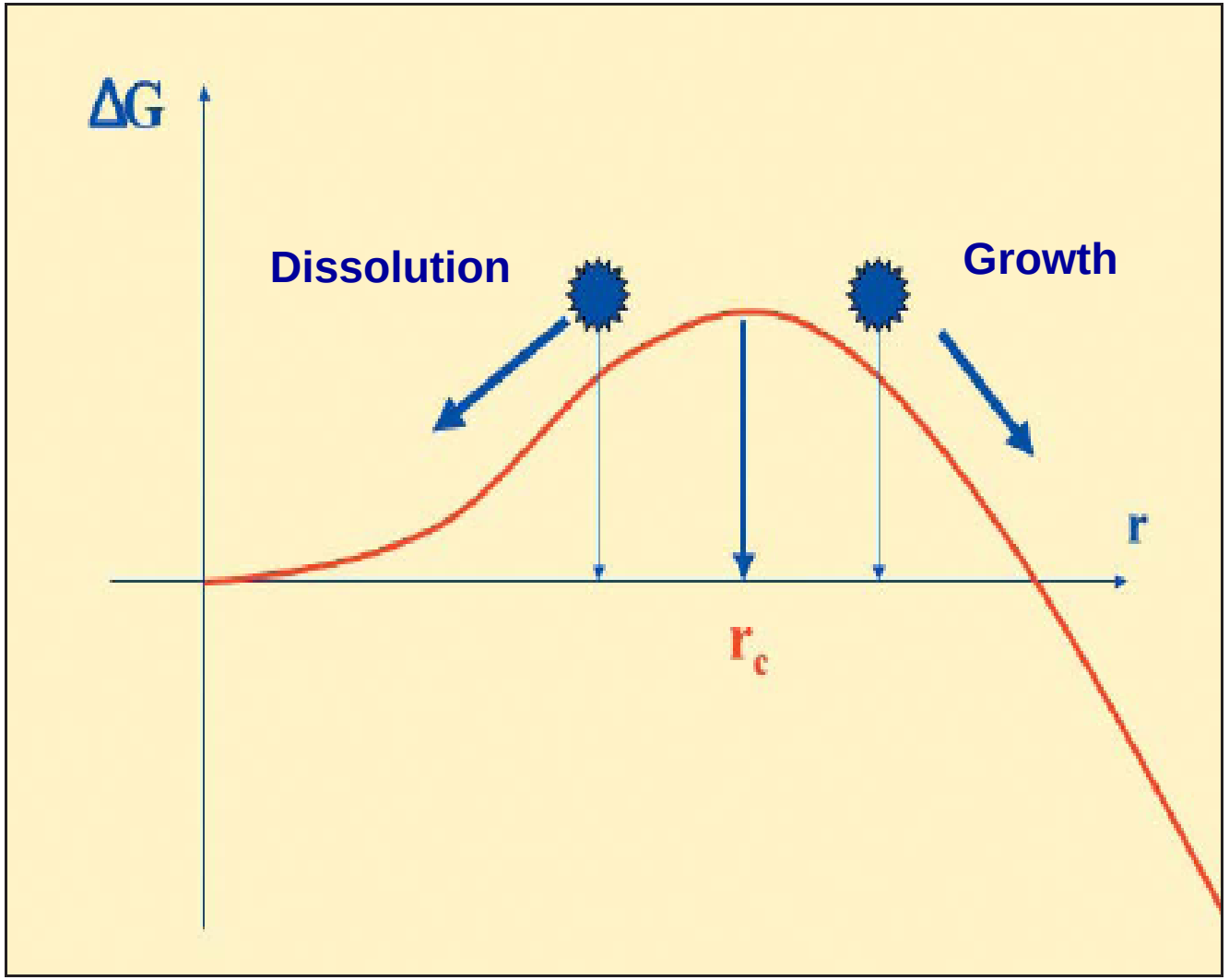
NUCLEATION



Time of induction of nucleation: Matitol < Sucrose < Trehalose

Frequency of Nucleation: Matitol > Sucrose > Trehalose

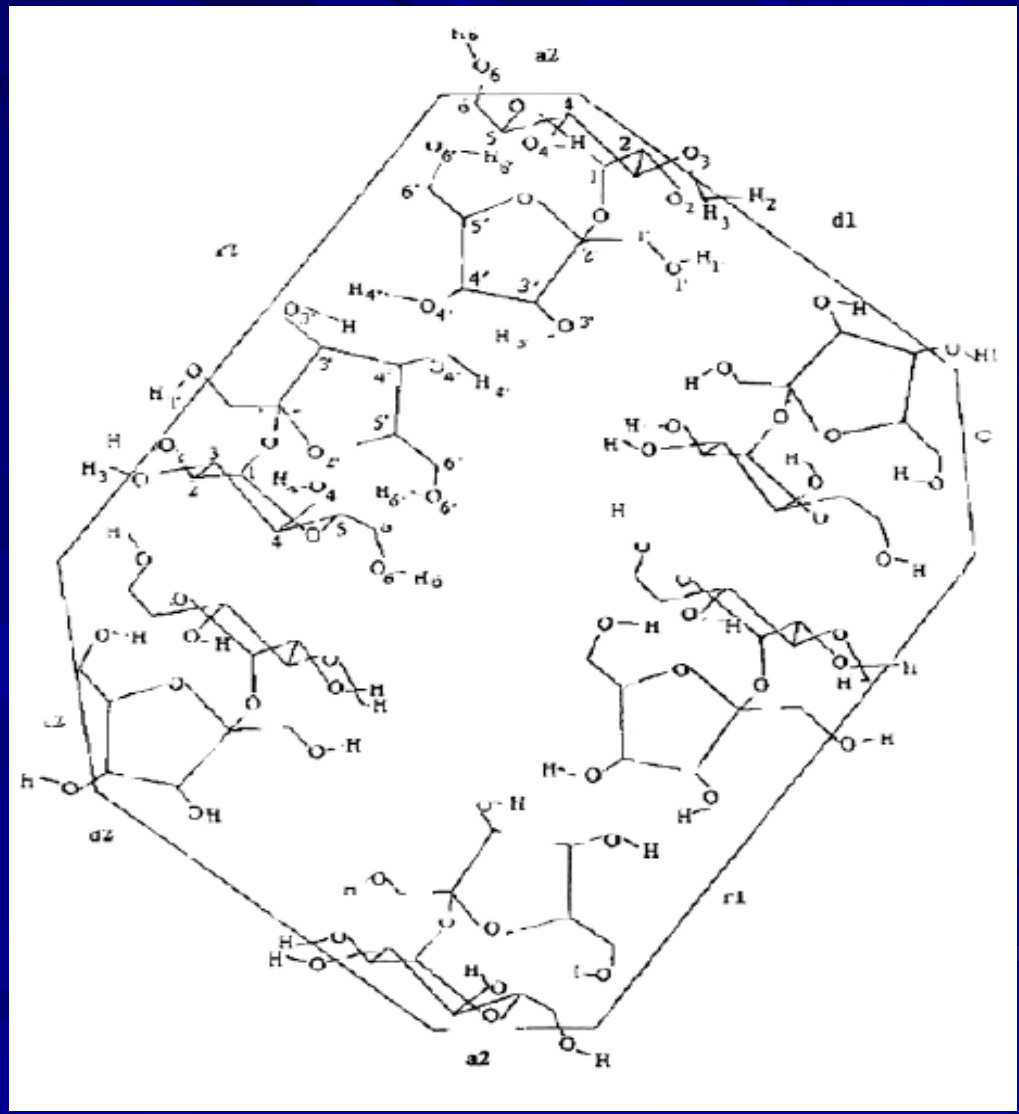
NUCLEATION



NUCLEATION

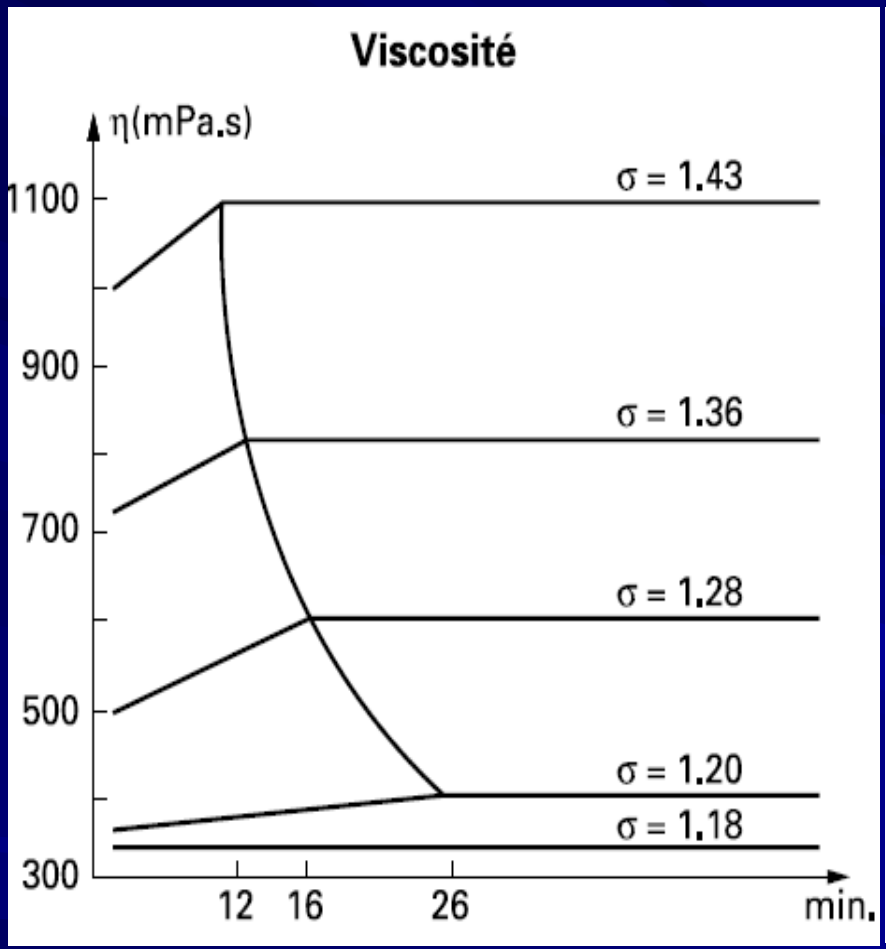
$$J = \frac{KT}{h} \exp\left(\frac{\Delta S}{R}\right) \cdot \exp\left(\frac{-\Delta H}{RT}\right)$$

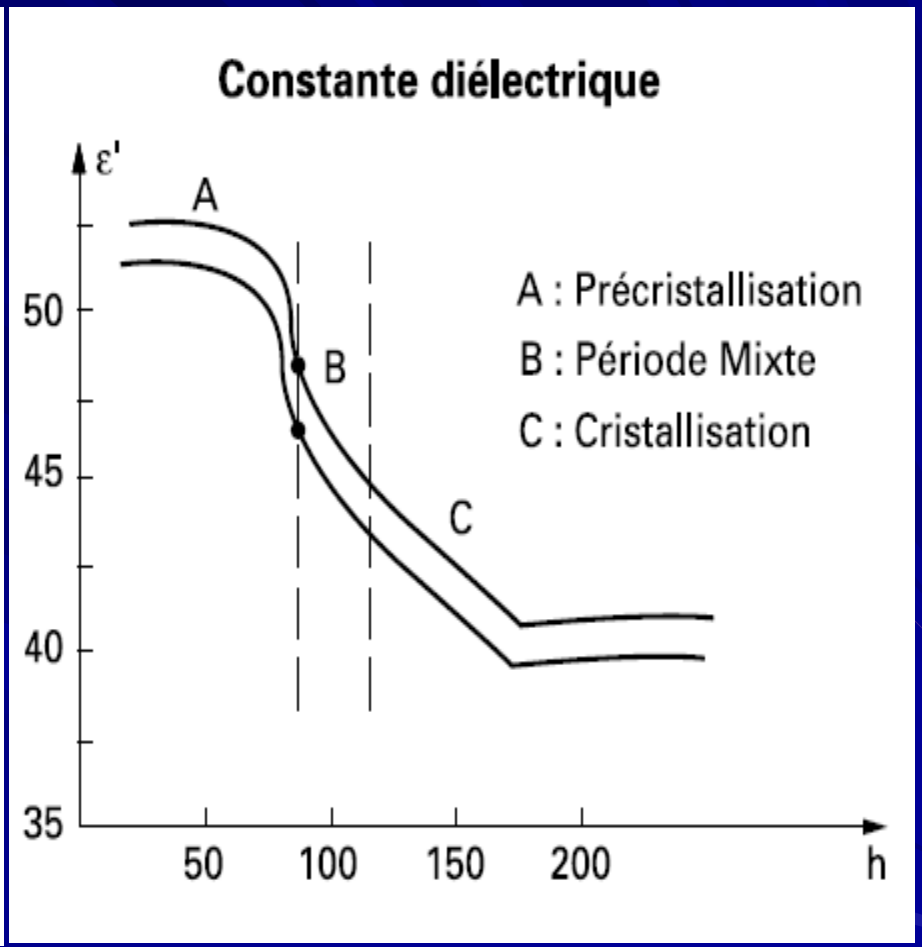
$$A_1 + A_1 \Leftrightarrow A_2$$
$$A_1 + A_2 \Leftrightarrow A_3$$
$$\cdot$$
$$\cdot$$
$$\cdot$$
$$A_{n-1} + A_1 \Leftrightarrow A_n$$



Hexamers of sucrose formed prior to the appearance of a nucleus for n = 80 – 100 molecules

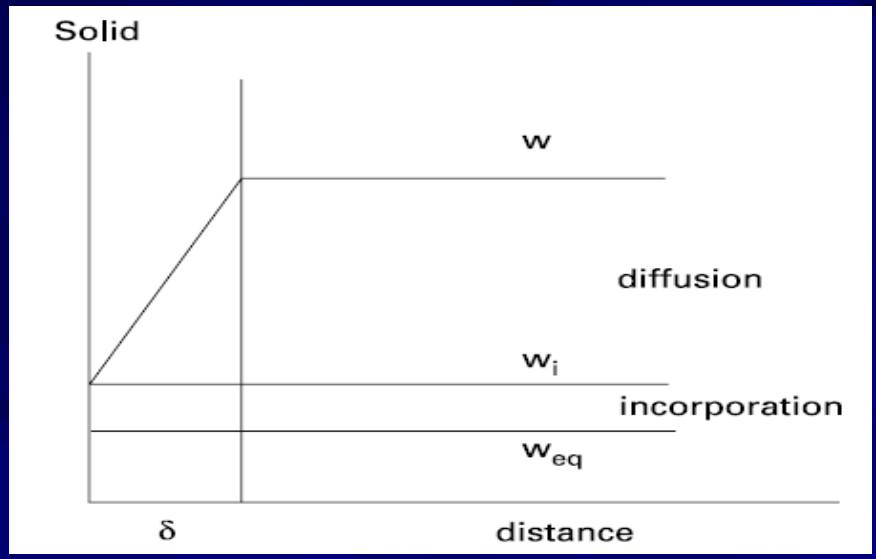
PRE-NUCLEATION EVIDENCE IN SUPERSATURATED SOLUTIONS



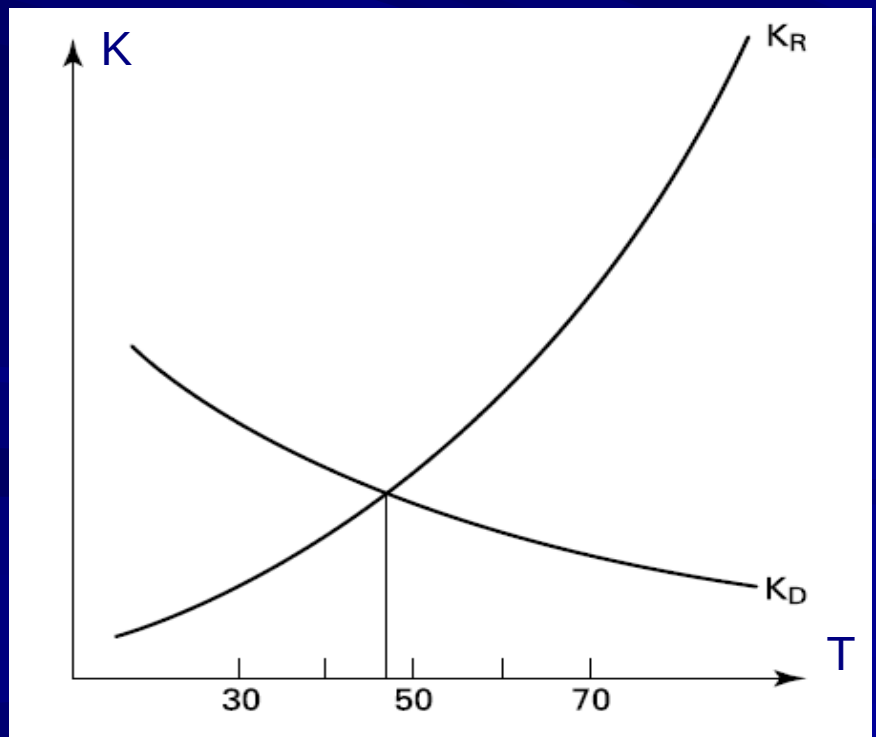


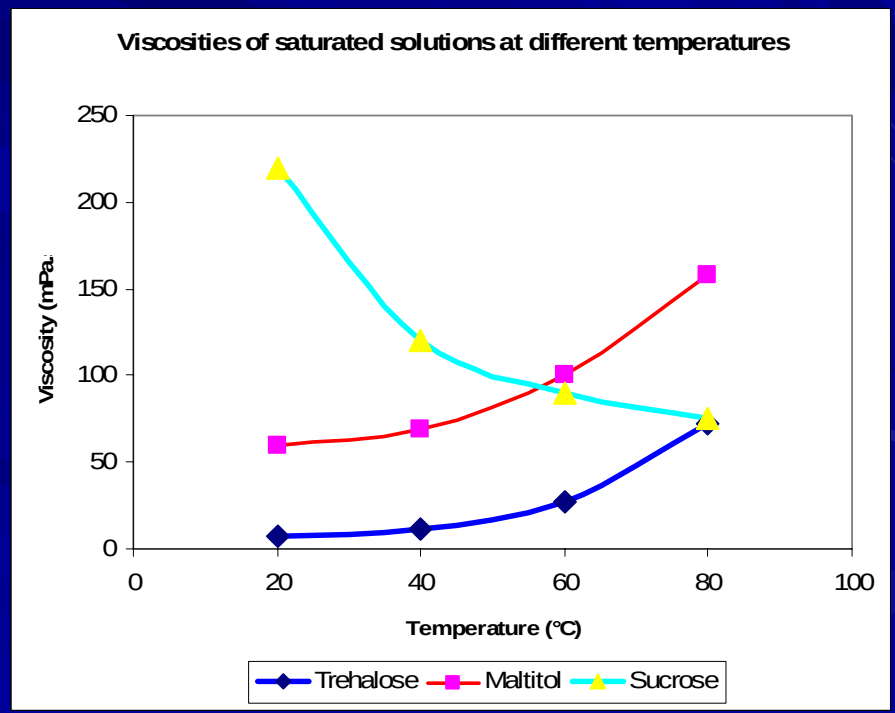
Tikhomiroff N., Industr. Alim. Agric. 82 (1965) 755-772.

CRYSTAL GROWTH RATE

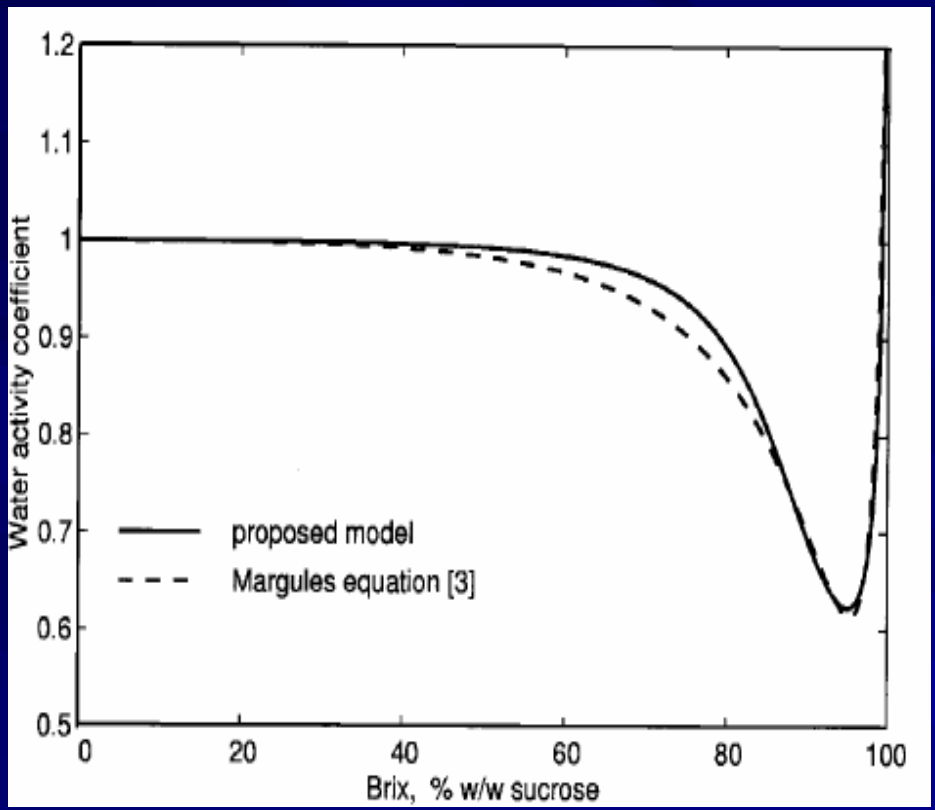


$$V = \frac{(C - C_0)}{\frac{d}{K_D} + \frac{1}{K_R}}$$





ROLE OF WATER IN CRYSTALLIZATION



Starzak, M. and Peacock, S.D.: *Zuckerind.* **123:** 433-441 (1998).

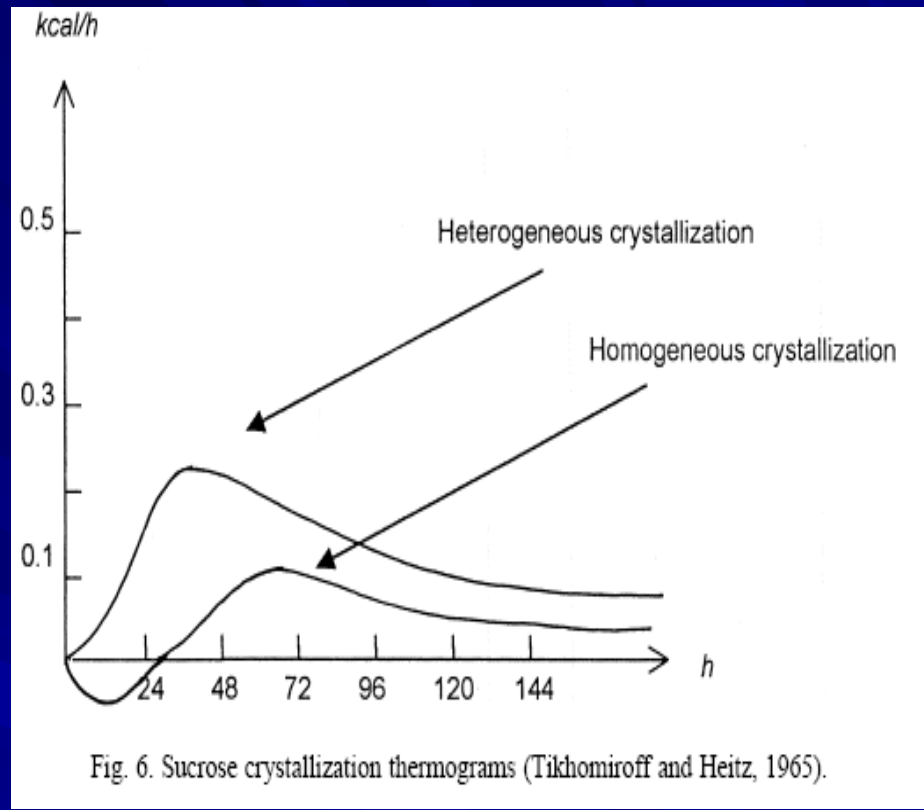


Fig. 6. Sucrose crystallization thermograms (Tikhomiroff and Heitz, 1965).

Tikhomiroff N., Heitz F.1965, pp. 341-355

Release of water molecules at the crystal – solution interface: f_w >1 for C > 97%

Endotherm at the beginning of crystallization: corresponds to water disassociation

Concentrated Amorphous Solution Nucleation

Preparation of CAS:

- Rapid cooling (-18°C) of concentrated (85% (w/w) disaccharide solution obtained by dissolution at T> 85°C
  Conservation of CAS 24 h at – 18°C
  No Crystallization

NUCLEATION OF CAS:

- Slow Heating (5°C/h)
- Visual Observation of First Crystals

TREHALOSE: T_N = 45°C (middle of sample) – rapid growth at rt

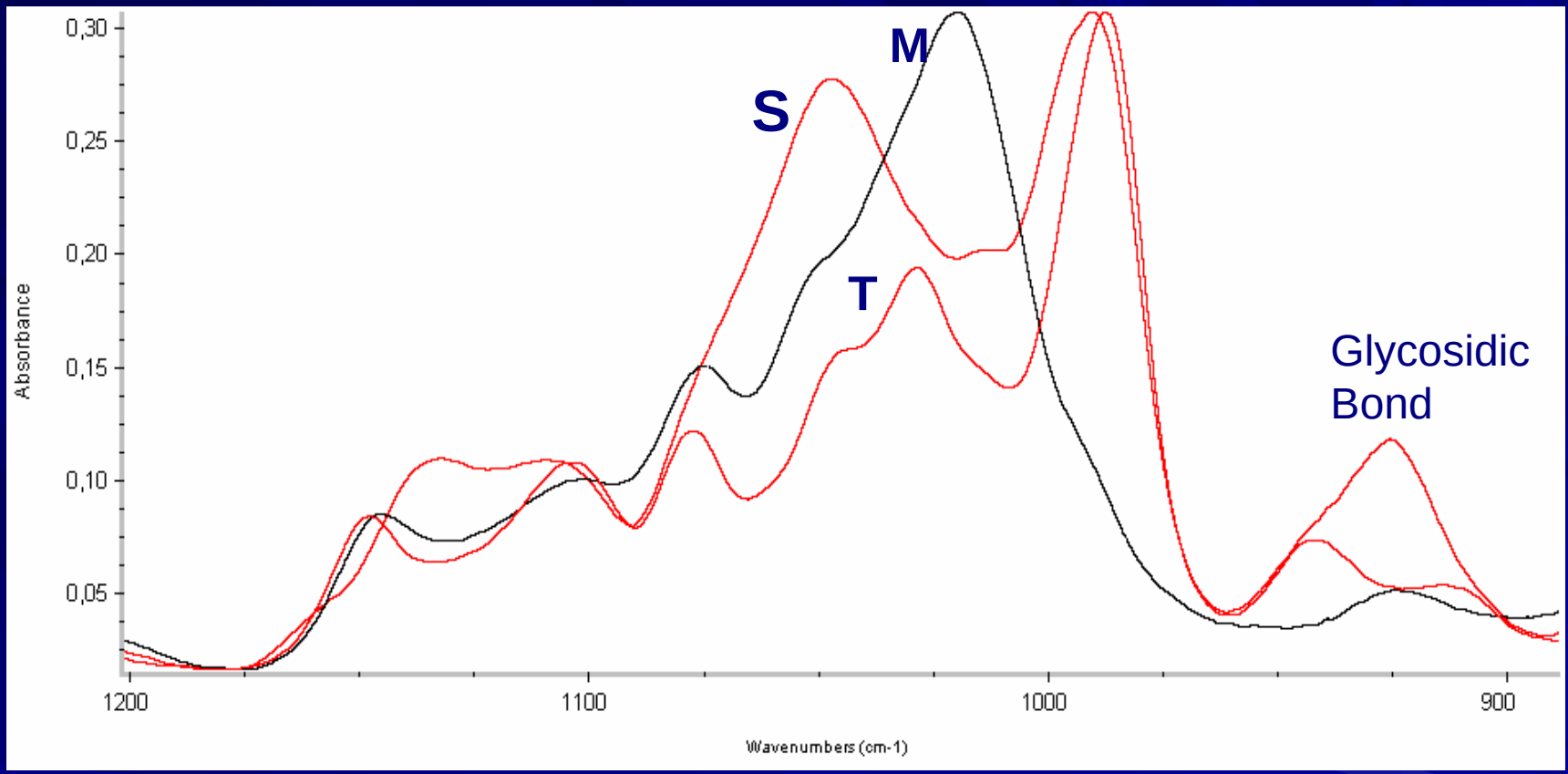
MALTITOL: T_N = 25°C (surface) – very slow growth at rt

SUCROSE: T_N = 15°C (dispersed) – slow growth at rt

FRAGILITY OF CAS FROM Tg – T_N:

TREHALOSE (70) > SUCROSE (45) > MALTITOL (29°C)

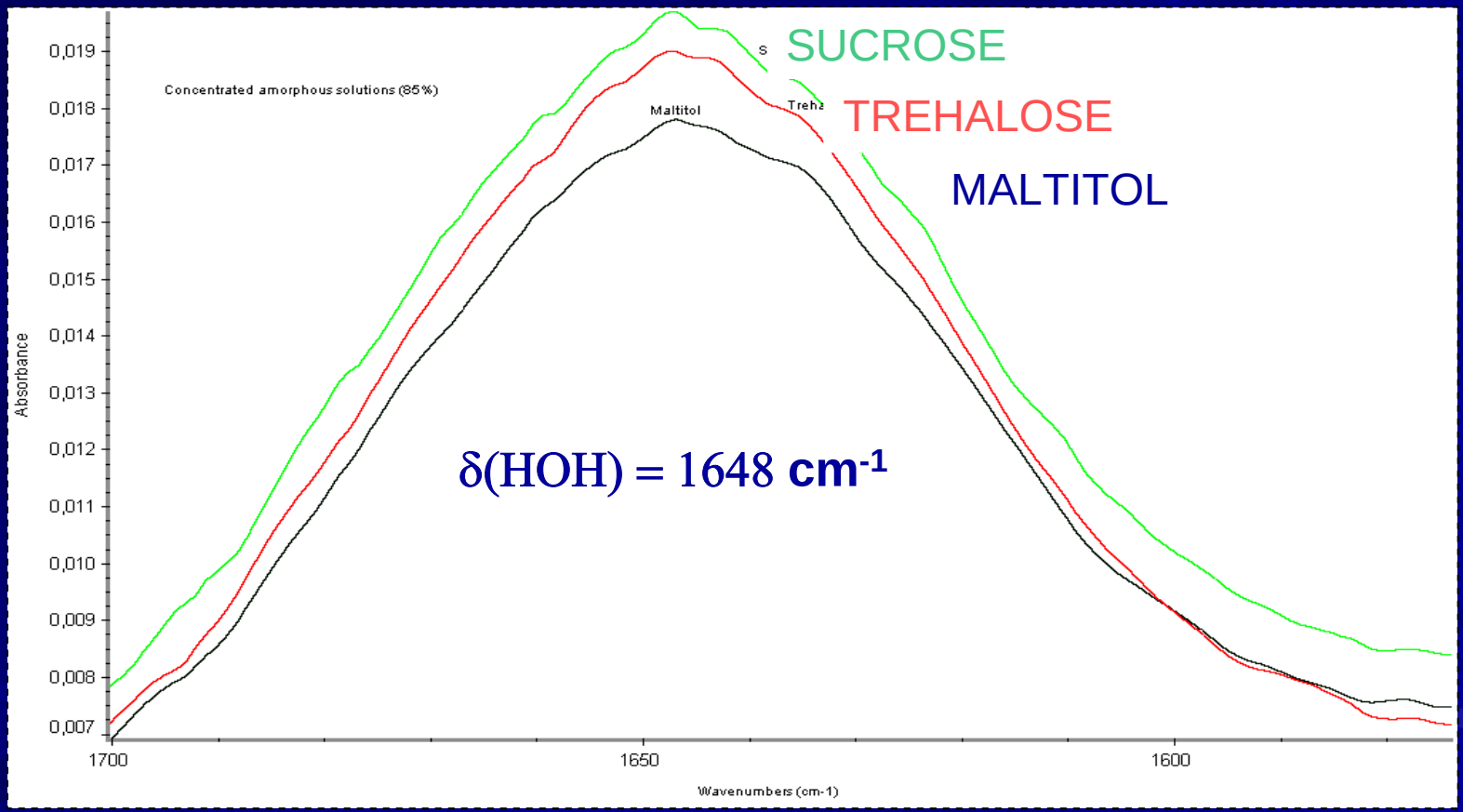
Concentrated Amorphous Solution FTIR



Folding of Glycosidic Bond: Sucrose > Trehalose
Sugar-Sugar interactions: Maltitol>Sucrose>Trehalose

Concentrated Amorphous Solution FTIR

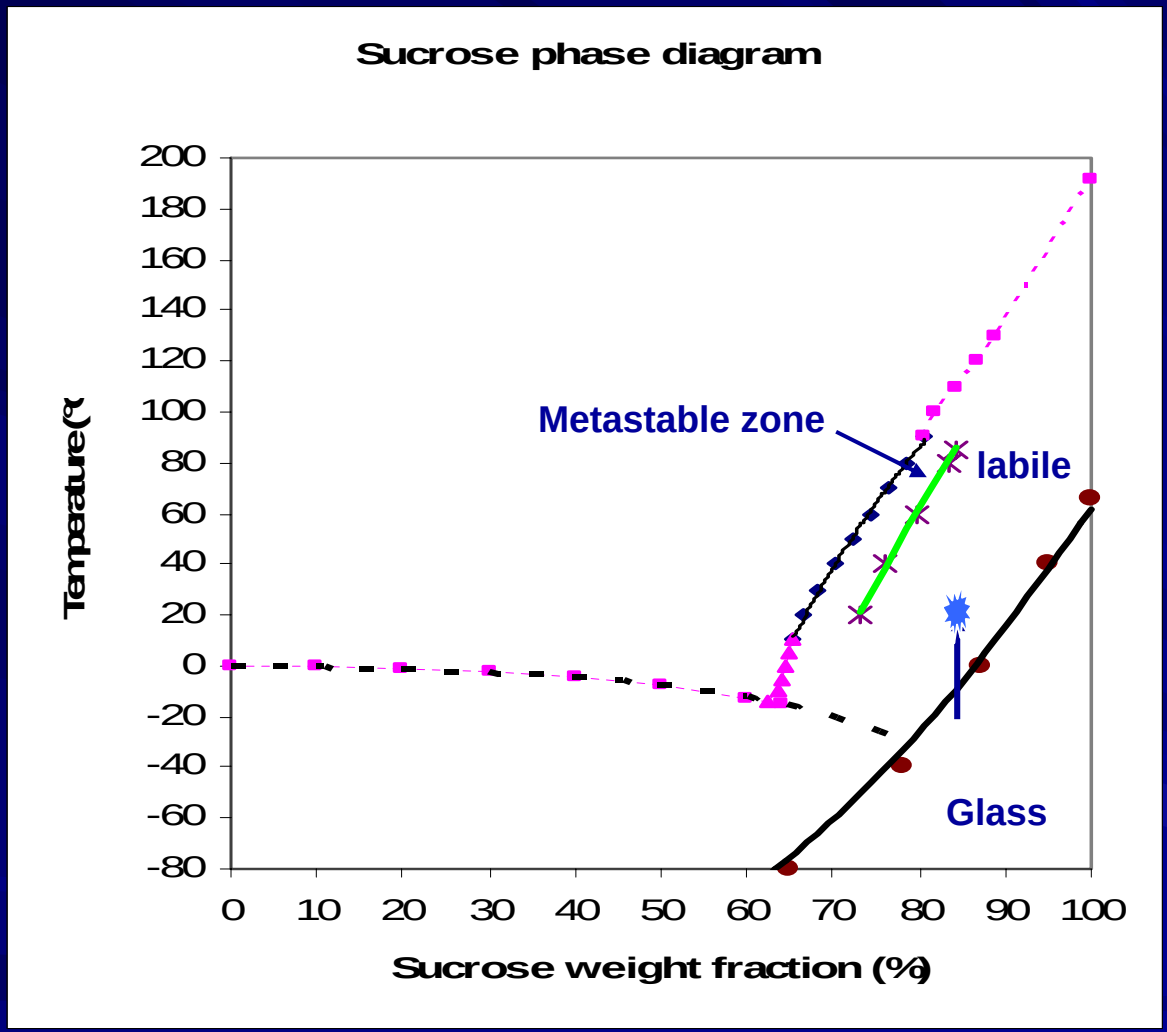
H_2O bending



WATER BINDING SIMILAR FOR 3 DISACCHARIDE CAS

(Hydration of Sugar Clusters)

Phase Diagram revisited: Sucrose



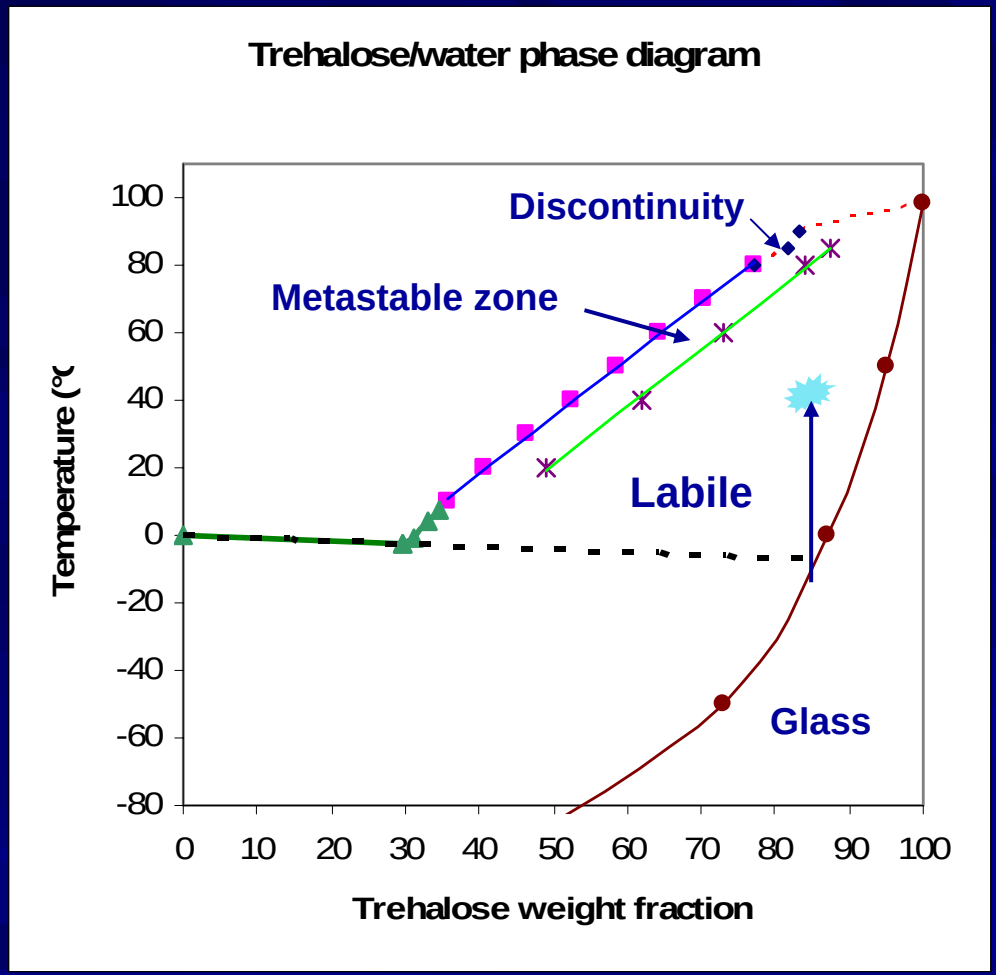
Metastable zone: High Mobility: Nucleation and Crystal growth

Labile zone : Mobility restricted, Nucleation difficult No Growth

CAS Nucleation: at 15°C – Slow Growth

----: Bubnik & Kadlec, in Sucrose(M. Mathlouthi and P. Reiser Eds.), 1995,
——— Tg: Y. Roos and M. Karel, (1991) J. Food Sci.Technol. 26,553 - 556

Phase Diagram revisited: Trehalose



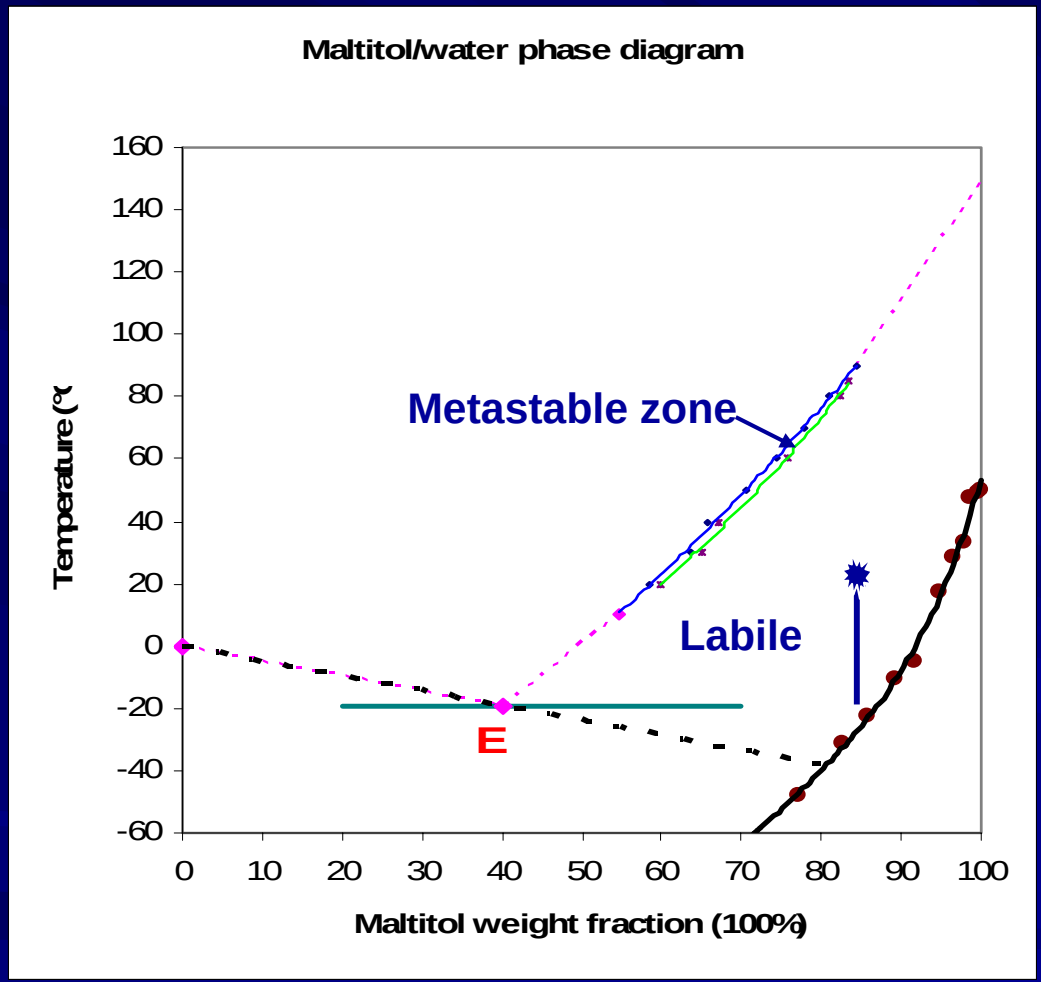
Discontinuity in Solubilty at 85°C: Polymorphism

Large Labile Zone: Relatively easy nucleation

Crystallization of CAS (85%) on heating from -18 to + 45°C Growth at room T°

---- Miller, de Pablo and Corti,Pharm. Res., 14 (1997) 578 – 590.
—— Chen, Fowler and Toner, Cryobiology, 40 (2000) 277 – 282.

Phase Diagram revisited: Maltitol



Narrow Metastable Zone: High probabilty of Nucleation

Existence of Eutectic Easily obtained experimentally

CAS Nucleation: Difficult – High viscosity- Very Slow Growth

— Siniti, Jabrane and Létoffé, Thermochimica Acta, 325 (1997) 171 - 180

CONCLUSION

COMPARATIVE SOLUTION PROPERTIES:

- Conformation Flexibilty: Sucrose > Trehalose (Maltitol lateral motion)

-Water Solubility : Sucrose > Maltitol > Trehalose (below 60°C)
Maltitol > Sucrose> Trehalose (above 60°C)

- Viscosity f(% mass): Maltitol > Sucrose > Trehalose

CRYSTALLIZATION CONDITIONS IN SOLUTION:

- Metastable zone width: Trehalose > Sucrose > Maltitol

- Nucleation Frequency: Maltitol > Sucrose > Trehalose

CONCENTRATED AMORPHOUS SOLUTION:

- Ease of Homogeneous Nucleation: Trehalose > Sucrose> Maltitol
- Viscosity of CAS : Maltitol > Sucrose > Trehalose
- Glass Fragility (of the CAS): Trehalose > Sucrose> Maltitol

PHASE DIAGRAM REVISITED:

- Differences in molecular mobility of Disaccharides in Metastable and labile zones revealed by Nucleation of CAS


THANK YOU
250 µm