Using solvent additives in melt crystallization of high-viscous organic mixtures

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Introduction

Down stream purification processes plays an important role in production of **value-added biochemicals**. Development of such process requires knowledge of material attributes and characteristics of their mixture which can limit the efficiency of conventional separation techniques. The aim of this work is to identify and remove barriers in production of highly pure glycols associated with close boiling components and their thermodynamic properties by **developing a solvent-aided melt crystallization process** to be integrated with distillation separation technique.

Methods

❖ **Role of mass and heat transfer** on crystal growth kinetics in a lab-scale cold finger crystallizer is estimated by the following method:

- Total driving force for crystal growth kinetics:

$$\Delta T_{tot} = (T_b^* - T_i^*) + (T_i - T_b) + (T_e - T_i) = G\left(\frac{1}{\Phi k_L} + \frac{\Delta H \rho_i}{h} + \frac{1}{k_r}\right)$$

- **Assumptions** :1) Surface tension is neglectable over the effect of mass transfer due to the low fluid velocity at natural convection 2) $T_i^* \approx T_e$

- Simplified equation for the crystal growth rate:

$$G = \frac{T_b^* - T_b}{\frac{1}{\Phi k_L} + \frac{\Delta H \rho_i}{h}}$$

Mass transfer resistance ($\frac{1}{\Phi k_L}$); Heat transfer resistance ($\frac{\Delta H \rho_i}{h}$)

Results and discussions

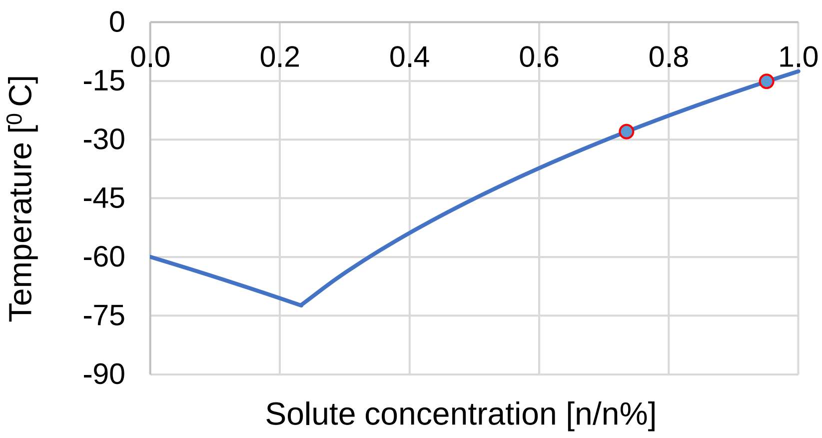

Figure 1. The equilibrium temperatures were estimates using UNIFAC-DMD predictive model (Thermodynamic properties optimized via FactSage software).

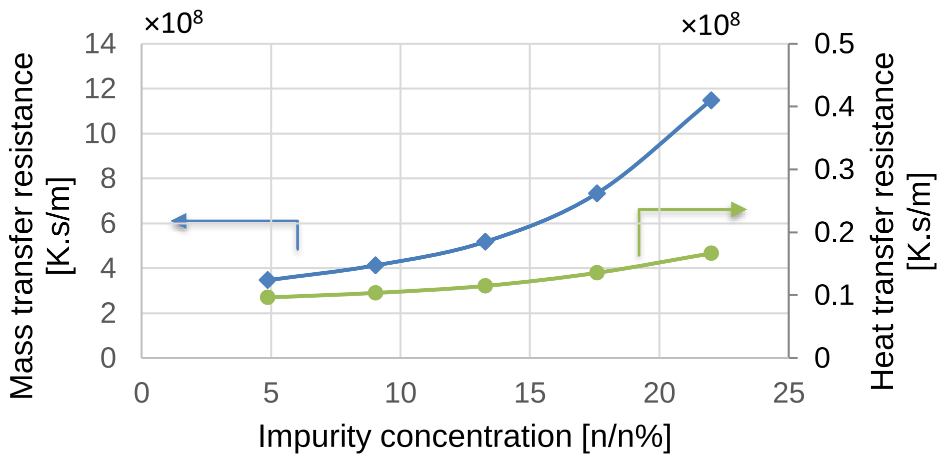

Figure 2. Dominating factor of crystal growth based on thermodynamic property simulations with Aspen plus V11.0 software for a binary glycol mixture.

- Among the physical properties of the material that affect mass transfer are viscosity and diffusion coefficient, both are temperature and solution composition dependent. Addition of solvent alleviate the effect of high viscosity at low operating temperatures.

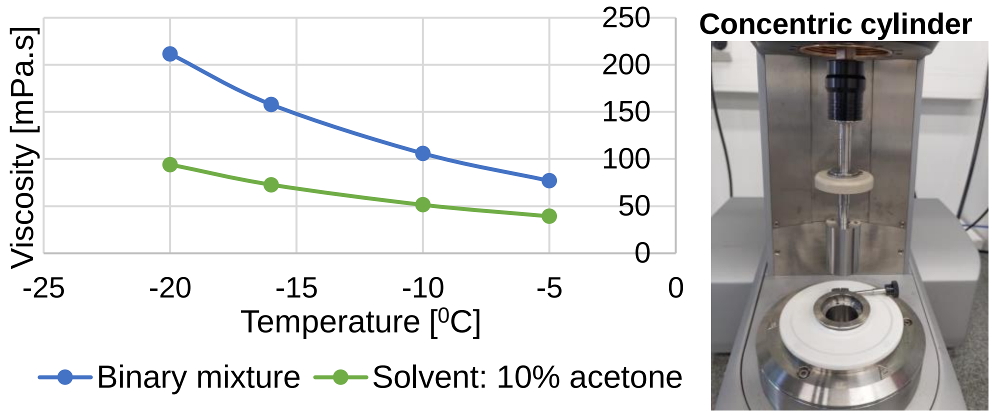

Figure 3. Dynamic Viscosity measured via Anton Paar Physica MCR 301 rheometer

- Addition of solvent can alter crystallization temperature, density gradient, nucleation rate, crystal growth and surface tension between the melt and crystal surface.

Table 1. Influence of acetone quantity on crystallization temperature.

Solution	Crystallization temperature [°C]
Binary mixture (95 n/n%)	-15.1
Solvent: 10 n/n% Acetone	-19.5
Solvent: 20 n/n% Acetone	-23.2

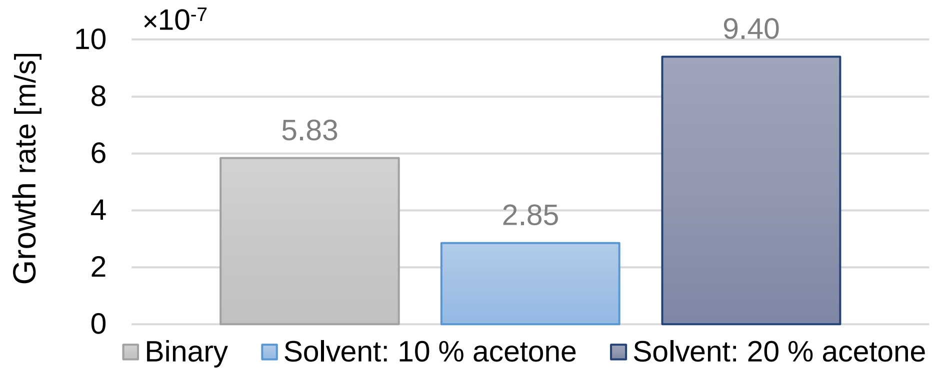

Figure 4. Growth rate measured in static beaker (inner diameter 33 mm) immersion set up with 3 °C supercooling degree.

Conclusion

- Although heat transfer phenomenon plays a major role in crystallization from melts, also mass transfer can become a dominating factor.
- Addition of the solvent can enhance the mass transfer and crystal growth when reduction in distribution coefficient is dominant over the interruption of solute incorporation into the crystal due to solvent interactions with the crystal surface.
- For further development of the crystallization process, the impact of solvents on product purity, process yield, crystal growth kinetics under optimum operational condition are being under consideration.

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