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Simulation and Empirical Studies of Solvent Evaporation Rates in Vacuum Evaporation Crystallization

Simulation results for continuous vacuum evaporation crystallization obtained by Aspen Plus and experimental results for semi-batch vacuum evaporation crystallization are presented. In the crystallization experiments, the fixed heat duty was used to compare the water evaporation rates and crystal properties obtained at different pressures. The solution selected was aqueous glycine. It has the ability to form a number of different crystalline polymorphs, which allows it to exhibit a variety of different physical properties while maintaining its chemical properties. X-ray diffraction results demonstrated that mainly the γ -crystal form is produced under the conditions applied in vacuum evaporation crystallization.

Keywords: Evaporation rate, Glycine, Simulation, Vacuum evaporation crystallization

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1 Introduction

Evaporation crystallization is a widely used crystallization method for relatively soluble substances in fine and bulk chemical industry, pharmaceutical industry, and food industry [1]. In evaporation crystallization, the solvent is partially separated from the solution by applying a sufficient amount of heat, so the solute crystallizes out from the solution in a solid form. The challenge in evaporation crystallization technologies is the energy consumption: the lower the energy consumption, the better the technology. To minimize the energy demand in evaporation crystallization, a number of technological breakthroughs have been made in the past few decades [2].

However, the evaporation kinetics related to momentary supersaturation levels has not been comprehensively investigated. This is especially relevant because, compared to batch cooling crystallization, batch evaporation crystallization is usually considered a more demanding process due to the difficulties in appropriately controlling the supersaturation level. The vapor pressure of solvent at different temperatures is one of the key factors in evaporation crystallization: the higher the vapor pressure, the higher the evaporation rate of the solvent.

Glycine is widely used for food, cosmetics, and pharmaceutical applications [3]. It has the ability to form a number of different crystalline polymorphs, which allows it to exhibit a variety of different physical properties while maintaining its chemical properties [4]. Various cooling or evaporation crystallization methods have been proposed as a production method for glycine [5, 6]. In evaporation crystallization, process conditions like temperature and pressure have a great impact on solvent evaporation rates, the supersaturation level, and crystal formation. Thus, to be able to control the quality of the final product, e.g., crystal shape, crystal size distribution, etc., and

optimize the crystallization conditions in terms of separation and energy efficiency, it is important to identify the most important process parameters that may affect product quality. In our previous work, we empirically studied the evaporation rates at different crystallization conditions [7]. The present work focuses on mass and energy balance calculations of evaporation crystallization based on thermodynamic modeling with the aid of Aspen Plus simulation as well as experimental work.

The objective of this paper was to gain deeper understanding on an evaporation crystallization process from aqueous solutions. The model compound chosen was glycine. Aspen Plus simulation software was used to simulate the continuous vacuum evaporation crystallization process. To validate the Aspen results, experimental results conducted in a semi-batch vacuum evaporation crystallizer at the same underpressures and solution concentrations as used in the Aspen Plus simulations are presented.

Thermodynamic properties such as the boiling point of glycine aqueous solution at three different underpressure conditions (40, 60, and 80 mbar) was first estimated by using Aspen Properties, then the results were validated experimentally. Based on these data, an Aspen simulation model was built for determining the water evaporation rate and crystallization rate.

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2 Methodology

2.1 Materials

In this study, 99 % pure proteomics-grade glycine was used. Aspen Plus helped to simulate the vacuum evaporation crystallization process and the Aspen Properties toolbox was used to study the thermodynamic properties of the glycine-water system.

2.2 Experimental Method

The solubility data for glycine in water as a function of temperature were taken from the literature [8] and used for selecting the concentrations for preparation of the initial glycine solutions. An amount of 30 mL of the initial glycine solution, which was slightly below the saturation point at the boiling point at the specific underpressure, was poured into a glass reactor equipped with a magnetic stirrer. Boiling points of glycine solutions were measured at three vacuum pressures. In the experiments a round-bottomed flask with an inside diameter of 64 mm was used. Thus, the surface area of the reactor was 0.00322 m². The reactor was placed in a heating mantle with a maximum heating power of 110 W. A fixed heating power of 60 W was applied in the evaporation rate and crystallization studies.

The evaporated water was recovered in a condenser container filled with ice. A vacuum pump created the desired underpressure. A pressure gauge was connected via the condenser to measure the actual pressure of the system. Each boiling point test was repeated two times. Then, the average temperature was determined as the boiling point temperature of the solution at the specific pressure. Fig. 1 presents the image of the experimental setup.

Figure 1. Image of boiling-point experimental setup: (1) vacuum pump, (2) condenser, (3) pressure gauge, (4) thermometer, (5) magnetic stirrer, (6) heating mantle.

2.3 Aspen Simulation

Aspen Plus simulation software was used to simulate the continuous vacuum evaporation crystallization process of glycine solution at different pressures. The Aspen Properties toolbox was employed to study the thermodynamic properties of the glycine-water system. The boiling-point temperatures of saturated glycine solutions were measured and estimated by Aspen Properties. The NRTL thermodynamic model was used in the simulation models.

3 Results and Discussion

3.1 Boiling Point Determination of Glycine Aqueous Solution

In the evaporation crystallization processes, the boiling point is a critical parameter for designing the process. Thus, prior to modeling of the vacuum crystallization unit it was essential to study the behavior of the solution at different underpressures. Measured boiling points and those estimated by Aspen Plus are depicted in Fig. 3. The Aspen Plus results are perfectly consistent with the boiling point temperatures measured experimentally, showing only a small deviation.

Figure 2. Solubility data for glycine in water and the initial concentration of the feed.

Figure 3. Boiling point temperature for glycine solutions at various vacuum pressures estimated with Aspen Properties (Glycine Aspen) and obtained experimentally (Glycine Exper.).

The boiling point of an aqueous glycine solution increases with a rise in pressure. According to the result, at 40 mbar the saturated glycine solution boils at 30 °C, and at 60 mbar the saturated glycine solution boils at 37 °C. The highest boiling temperature was at 80 mbar, namely, 43 °C. In sum, the higher the pressure, the higher is the boiling temperature and the higher the solubility of the glycine solution.

3.2 Evaporation Rate

The evaporation rates of water ($\text{g}_{\text{water}} \text{s}^{-1}$) from an aqueous glycine solution at different underpressures were determined experimentally. To express the evaporation rate in a more general manner, the evaporation fluxes (in $\text{g}_{\text{water}} \text{m}^{-2} \text{s}^{-1}$) were determined by taking the evaporation surface area of the experimental system, i.e., the area of the upper liquid surface, into account as well. Fig. 4 displays the water evaporation fluxes obtained for aqueous glycine solutions and pure water as a function of vacuum pressure. Under these vacuum conditions, there is only a slight difference between the evaporation rate of the glycine solutions and pure water. Based on these results, the evaporation rate of glycine solution at an underpressure below 80 mbar could be considered similar to the evaporation rate of pure

Figure 4. Evaporation fluxes of pure water and aqueous glycine solutions.

water. Therefore, the presence of glycine molecules in the quantities of 26–30 g glycine/100 g water did not have a significant influence on water evaporation rates and fluxes.

3.3 Aspen Plus Simulation

To determine the energy and mass balance of vacuum evaporation crystallization of glycine, the continuous process was modeled with Aspen Plus. The mixed suspension-mixed product removal (MSMPR) crystallizer module was employed to model the continuous vacuum evaporation crystallization process. The module provides mass and energy balance calculations by assuming that the product magma leaves from the unit in equilibrium. The mass flow rate of the feed glycine solution was set to be 2.12 g min^{-1} and the initial temperature was 20 °C. Fig. 5 presents the Aspen Plus flow sheet for continuous vacuum evaporation crystallization of glycine.

To compare the simulation results, a semi-batch evaporation crystallization process was investigated with experimental conditions similar to those used in the continuous evaporation crystallization simulations. The initial glycine concentrations indicated in Fig. 2 were used both in the experiments and in simulations.

Three different underpressures, i.e., 40, 60, and 80 mbar abs, and a constant heat duty (60 W) were used to simulate the process. Fig. 6 illustrates the amount of water evaporated from the crystallizer as a function of pressure. The simulation results were consistent with the experimental results. At the studied underpressures, 60 % of the water in the feed was evaporated. However, the crystallization of the glycine solution is slower than the evaporation of water. Although 60 % of the water in the feed was evaporated at 40 mbar, only 40 % of the glycine in the feed was crystallized, leaving behind 60 % uncrystallized glycine (aqueous glycine) in the feed solution. Therefore, at 40 mbar, 60 W seems not to be enough to produce a large quantity of crystals. On the other hand, a higher crystallization rate occurred at 80 mbar. According to the experimental results, 2.76 g of crystals were produced at 40 mbar, 3.26 g at 60 mbar, and 4.91 g at 80 mbar.

Figure 5. Aspen Plus simulation flow sheet for vacuum evaporation crystallization of glycine at a pressure (abs) of 40 mbar and with a heat duty of 60 W.

Figure 6. Mass ratio of evaporated water and water in the feed obtained by Aspen Plus simulations for a continuous process and empirically in a semi-batch process with a heat duty of 60 W. In the semi-batch process, the solution had a mass of 31 g.

Fig. 7 compares the amount of solid crystals produced from the glycine solution experimentally with the Aspen simulation model.

Figure 7. Crystal yield of glycine from semi-batch experiments and Aspen Plus continuous process simulations with a heat duty of 60 W and solution mass of 31 g.

The amount of crystals produced experimentally seems to be slightly higher than the amount obtained from Aspen Plus calculations. According to the Aspen Plus calculations at 80 mbar, about 50 % of glycine in the feed solutions was crystallized, while experimental results shows that 60 % of the glycine was crystallized. However, in the Aspen model, a higher crystallization rate will be achieved by increasing the heat duty. Therefore, at a lower heat duty water vaporizes very rapidly, but the glycine solution crystallizes slowly.

The crystals will not suddenly form when the first drops of water evaporate. Instead, the crystallization process undergoes three sequences. When the underpressure is applied to the system, it becomes thermodynamically unstable. Then the pure water evaporates from the system leaving behind an aqueous solution of glycine with less water content. This lowers the free energy of the system, thus instantaneously the nucleation starts and glycine crystals start gradually to grow.

Fig. 8 illustrates the heat demand, both experimental and simulated, for vacuum crystallization of glycine solutions at three different underpressures. The crystallization process may

Figure 8. Specific heat power from semi-batch experiments and Aspen Plus continuous process simulations of aqueous glycine solutions at different underpressures.

be faster or slower, depending on the amount of heat input to the system. On the other hand, a longer residence time with low heat input leads to a slower crystallization process.

According to the isothermal semi-batch experimental results with a duration of 15 min, 13.41 kW of heat was required to produce one kg of crystals at 40 mbar, while at 80 mbar almost a half of that heat power per crystal quantity was required (7.54 kW kg⁻¹ solid). In the simulation of the continuous process, at 40 mbar a heat power of 22.88 kW kg⁻¹ crystals was needed, while at 80 mbar, 15.84 kW kg⁻¹ crystals was required. From Fig. 8 it can be concluded that the continuous process mode necessitates more heat power than the experimental isothermal semi-batch evaporative crystallization.

The thermodynamic model used in the simulation may be the cause of the heat demand deviation between experimental and simulation results. On the other hand, the Aspen Plus simulation was a continuous process while the experiment was a semi-batch process. The process mode was also different; therefore, they are not directly comparable.

3.4 SEM Images

Fig. 9 presents the pictures obtained by scanning electron microscopy (SEM) taken from the experimentally produced solid crystals at various underpressures. The difference in particle size can be observed from the image. Even the particles produced from the same test are not necessarily the same size. The largest particles are generated at 40 mbar, and when the pressure was increased to 60 or 80 mbar, the particle size seemed to decrease. Thus, the lower the pressure, the larger is the particle size.

The chord length distribution (CLD) was measured with a focused beam reflectance measurement (FBRM Particle Track, Mettler, Toledo). Fig. 10 illustrates the CLD of glycine crystals produced under these three underpressures. The crystals generated at 40 mbar have a slightly larger size compared to other crystals, while crystals produced at 80 mbar resulted in the smaller crystals.

a)

b)

Figure 9. SEM images from solid crystals produced at 40, 60, and 80 mbar: (a) scale 1 mm magnification: $\times 100$; (b) scale 100 μm , magnification: $\times 600$.

Figure 10. Chord length distribution for glycine crystals produced at 40, 60, and 80 mbar.

Figure 11. XRD patterns of the original glycine sample and glycine crystallized from aqueous solutions at 40, 60, and 80 mbar.

3.5 Structure Analysis of the Crystals

X-ray powder diffraction (XRD) was applied to analyze the crystal structures of glycine produced at 40, 60, and 80 mbar. Fig. 11 displays the XRD patterns of the glycine crystals. The XRD patterns were collected at ambient temperature and pressure with a Bruker D8 Advance diffractometer. The voltage and current were 40 kV and 20 mA, respectively. Patterns were recorded over a $2\theta^\circ$, using a step size of 0.013° . XRD analysis proved that the obtained glycine crystals were mainly in the γ -form, but some α -form crystals were also detected.

4 Conclusions

The effect of different underpressures on the crystallization of glycine aqueous solution was investigated both experimentally and via simulation. Three pressures were applied, namely, 40,

60, and 80 mbar, both in the experiments and in the simulation.

According to both experimental and simulation results, the crystallization of glycine solutions is slower than the evaporation of water. For instance, at 40 mbar 60 % of the water in the feed was evaporated, but only 40 % of the glycine in the feed was crystallized, leaving behind 60 % uncrystallized glycine in the feed solution. On the other hand, the amount of solid crystals produced experimentally was slightly higher than that of the Aspen model. According to the Aspen model, at 80 mbar about 50 % of glycine in the feed solutions would be crystallized but the experimental results indicated that up to 60 % of the glycine was crystallized. Therefore, at 40 mbar and 60 W seem not to be enough to produce a large quantity of crystals. By raising the heat duty in the model, the amount of crystals will increase.

According to the isothermal semi-batch experimental results with a duration of 15 min, 13.41 kW of heat was required to produce one kg crystals at 40 mbar, while at 80 mbar almost a half of that heat power per crystal quantity was required, i.e., 7.54 kW kg⁻¹ solid.

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The authors have declared no conflict of interest.

Abbreviations

CLD	chord length distribution
FBRM	focused-beam reflectance measurement
MSMPR	mixed suspension-mixed product removal
SEM	scanning electron microscopy
XRD	X-ray powder diffraction

References

- [1] B. Y. Shekunov, P. York, *J. Cryst. Growth* **2000**, 211, 122–136. DOI: [https://doi.org/S0022-0248\(99\)00819-2](https://doi.org/S0022-0248(99)00819-2)
- [2] L. Haijiao, W. Jingkan, W. Ting, W. Na, B. Ying, H. Hongxun, *Chemosphere* **2017**, 173, 474–484. DOI: <https://doi.org/10.1016/j.chemosphere.2017.01.070>
- [3] A. M. Alabanza, M. Mohammed, K. Aslan, *Nano Biomed Eng.* **2013**, 5 (4), 140–147.
- [4] M. Matsumoto, Y. Wad, A. Oonak, K. Onoe, *J. Cryst. Growth* **2013**, 373, 73–77. DOI: <https://doi.org/10.1016/j.jcrysgro.2012.11.022>
- [5] M. A. Pinardi, K. Aslan, *Cryst. Growth Des.* **2010**, 10, 4706–4709. DOI: <https://doi.org/10.1021/cg101059c>
- [6] J.-Q. Liu, Z.-L. Xu, K.-G. Zhou, *J. Membr. Sci.* **2004**, 240 (1–2), 1–9. DOI: <https://doi.org/10.1016/j.memsci.2004.03.027>
- [7] J. Puranen, M. Louhi-Kultanen, in *Proc. of the 23rd Int. Workshop on Industrial Crystallization* (Eds: H. Lorenz, H. Buchholz), Magdeburg **2016**.
- [8] J. W. Mullin, *Crystallization*, 4th ed., Butterworth-Heinemann, Oxford **2001**.

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