

A Deterministic Formulation and on-line monitoring technique for the Measurement of Salt Concentration in Non-Isothermal Antisolvent Crystallization Processes

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A complete framework to measure and anticipate the salt concentration during crystallization process is presented. On-line monitoring of the solute concentration based on conductivity of the solution is implemented. The conductivity of the dissolved compound is dependent on its concentration in the solvent and temperature. Therefore, a calibration test is applied and an experimental exponential model of concentration as a function of conductivity is developed in the whole operating range of antisolvent feed rate and temperature. A deterministic model which can predict the behaviour of the amount of salt with respect to the crystal growth parameter is introduced. To validate the model and assess the merits of the proposed strategy, the crystallization of sodium chloride in water using ethanol as antisolvent is performed in an experimental bench-scale semi-batch crystallizer.

1. Introduction

Crystallization process is one of the key unit operations in the food, pharmaceutical and fine chemical industries. It is the most common way of producing high value chemicals of high purity and desired particle size and shape. Characterizing the crystallization phenomenon cannot be achieved without measuring and anticipating the solute concentration changes. Concentration measurement provides information regarding the dynamic of the solute mass transfer and crystal growth. Any method to monitor and predict the concentration changes can improve understanding and controlling the underlying mechanisms such as nucleation and growth. Salt concentration measurement is necessary to calculate supersaturation which is the main driving force in crystallization process. By measuring the concentration, supersaturation can be monitored by incorporating the equilibrium concentration. Controllability of supersaturation affects significantly the crystal characteristics.

To achieve this, a comprehensive crystallization modelling framework and an on-line in situ method of concentration measurement is developed in this article. In previous (Galan et al. 2010, Stochastic approach for the calculation of antisolvent addition policies) (Cogoni et al, 2013, Prediction of the asymptotic CSDs) it was shown that by using a novel stochastic approach the particle size distribution (PSD) time evolution in non-isothermal antisolvent crystal-growth process can be obtained and global model with the direct dependencies on the manipulated variables (antisolvent feed rate and temperature) was presented. In this framework, solute concentration behaviour is also characterized during the process. In the first step, an on-line in-situ measurement technique based on conductivity of the solution is introduced in order to monitor the salt concentration. This technique focuses on the ions when dissolve in the solvents. It is suitable for high-concentration crystallization operations when most other sensors would fail. The salt concentration is measured by determining both temperature and conductivity of the solution which are then translated into the concentration. A deterministic model which can predict the behaviour of the amount of salt with respect to the growth parameter that has already been determined (Cogoni et al. 2013a, Prediction of PSD in nonisothermal antisolvent crystallization) is developed. In this way we could consider the CSD affects the salt consumption.

To validate the proposed strategy, non-isothermal crystallization of sodium chloride using ethanol as antisolvent was considered where a set of experiments for the nine temperature-antisolvent flowrate combinations was performed and the results from the model were compared with the experimental data at different time of the batch.

2. Experimental set-up

A laboratory scale software/hardware framework to measure the solute concentration for this case study was set up. At the startup condition, the crystallizer which is a 1 l Erlenmeyer flask loaded with an aqueous solution of NaCl made up of 34 g of 99.5 % pure NaCl (Sigma, United States) in 100 g of deionized water. The reactor is immersed into an isothermal temperature bath and the temperature is measured using an RTD probe that is wired up to a slave temperature control system capable of heating and cooling. A stirrer at the speed of 400 RPM provides the reactor mixing. Ethanol with reagent grade of 190 proof is added with a constant flow rate to the stirred solution using a calibrated peristaltic pump (Cole Parmer, United States). The master control is performed by a computer control system that is wired up to the slave temperature and flow-rate controllers. The desired set-points are set by the master controller. All relevant process variables are recorded.

During the experiment, solution is pumped out and the conductivity is measured using an Orion 4 STAR conductivity meter and probe of model 018020 MD. Data is transmitted and recorded On-line. The concentration of the solution is measured by simultaneously measuring the solution conductivity, temperature and ethanol mass fraction. All process variables are recorded using a computer data acquisition and control system. A schematic of the experimental set up and all instrumentation is displayed in Figure 1.

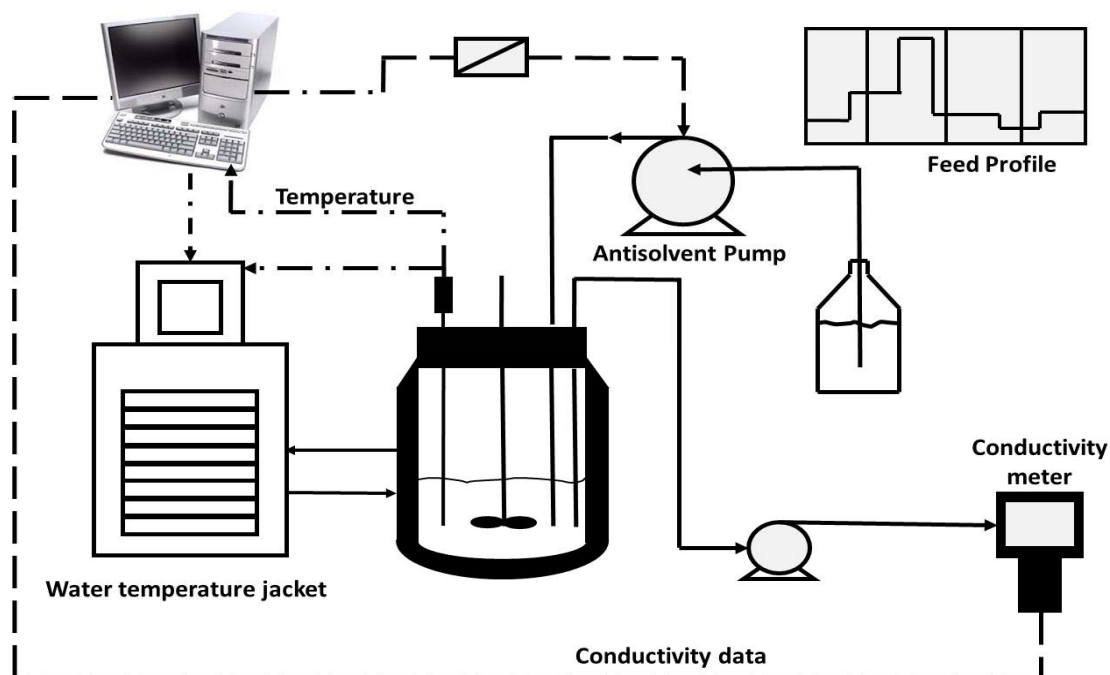


Figure 1: Schematic of apparatus and sensors used in this work

2.1 Solution concentration inference

There are various methods that have been reported in the literature for the measurement of solution concentration which includes from expensive techniques such as refractive index measurement (Helt et al., 1977, Effect of temperature on the crystallization of potassium nitrate); (Sikdar et al., 1976, Magnesium Sulfate and Citric Acid Water Systems), densitometry (Garside et al., 1996, Continuous measurement of concentration); (Qiu et al., 1990, Batch stirred crystallizer), Fourier Transform Infrared (FTIR) Spectroscopy (Nagy et al., 2012, Advances in Crystallization Control) to alternative cheaper methods including the use of electrical conductivity (Hlozny et al., 1992, On-line measurement of supersaturation in batch crystallizer); (Liszi et al., 1987, Determination of Supersaturation Using Conductivity); (Nowee et al., 2007, Optimization in seeded

cooling crystallization). In this work the concentration of the solution is measured by simultaneously measuring the solution conductivity, antisolvent mass fraction and temperature. This represents an inferential measurement whereby the conductivity, antisolvent mass fraction and temperature are the primary measurements which are then translated into the secondary inferred measurement being the concentration. Solubility of sodium chloride is assumed to be independent of temperature in the small ranges. However, the conductivity of a solution increases with temperature, as the mobility of the ions increases. (Hayashi, 2004, Temperature-electrical conductivity relation) If the temperature T does not vary too much, a linear approximation is typically used:

$$\delta(T) = \delta_0 [(1 + \alpha(T - T_0))] \quad (1)$$

Where $\delta(T)$ is the conductivity at the measured temperature in mS/cm, α presents the temperature coefficient of resistivity, T_0 is a fixed reference temperature (20°C for this experiment), and δ_0 is the conductivity at the reference temperature T_0 . The parameter α is fitted from measurement data. Since the linear approximation is only estimation, α is different for different reference temperatures. Eq(1) is used to convert the conductivity of the solution at the temperature of the experiment to the value at the reference temperature (20 °C). At this temperature a series of solutions of aqueous ethanol at known concentrations (10, 20, 30, 40, 50, 60, 80 wt %) are prepared representing the concentration range of the crystallization experiment. The conductivities of these solutions are measured at various salt concentration range of crystallization. The data collected is shown in Figure 2. The conductivities of the various solutions increase with concentration until a point where the conductivity becomes independent of concentration. In fact when we reach the solubility equilibrium, rest of the salt that is added to the solution is deposited at the bottom of the reactor and does not contribute to the concentration of ions. Since the effect of salinity on dielectric constant and viscosity is negligible (Kestin et al., 1981, Dynamic and kinematic viscosity of aqueous NaCl Solutions), according to Debye-Huckel-Onsager theory, ions' concentration is the only factor that influences the conductivity of the solution which will be constant after equilibrium point. This point represents the limiting conductivity at which any further increase in conductivity is only possible by decreasing the ethanol weight percent. The locus of these points is tracked with an exponential model of concentration as a function of conductivity (Figure 3):

$$w = \left(1 - \exp\left(-\frac{\delta_0}{b}\right)\right) * a \quad (2)$$

a and b are constants with values 27 and 86. This equation is used to determine the salt weight percent at the measured conductivity which can then be converted to concentration regarding the amount of antisolvent added and the total volume of the solution.

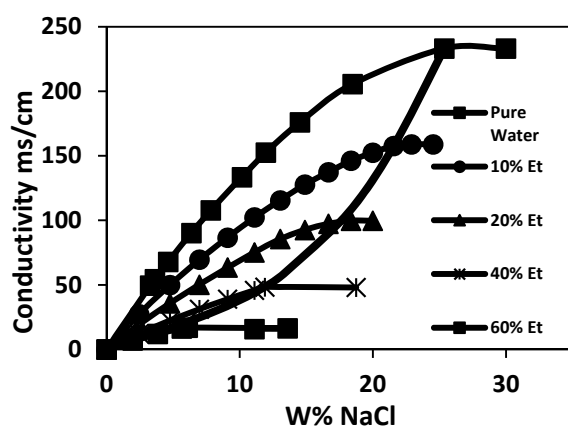


Figure 2: Conductivity of sodium chloride at various concentrations and ethanol mass fraction with the equation shown for the locus of limiting conductivity

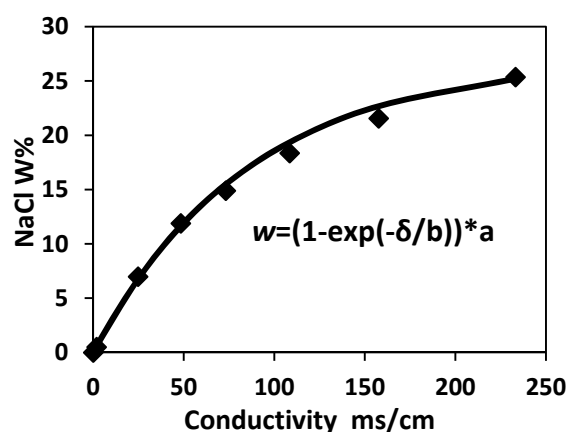


Figure 3: Sodium chloride mass percent vs the limiting conductivity

3. Modelling salt consumption in antisolvent crystallization

To characterize the dynamic behaviour of the salt consumption we assume amount of NaCl is linearly changed with time. Since the curve is reaching a final value (saturation around 7 g) at which the change in salt concentration with respect to antisolvent addition rate is almost negligible the following model is proposed:

$$\frac{dm}{dt} = -\frac{1}{\tau}(m - 7) = -\beta r(m - 7) \quad , m(0) = 34 \quad (3)$$

Where, $\tau = \frac{1}{\beta r}$ represents the inverse of the reaction rate coefficient and β is a parameter, to be evaluated that relates the quantity of salt consumed with the size of the crystals. The parameter, r , can be considered to be proportional to the one of the logistic equation where its dependency on the antisolvent flow rate and temperature is linear (Cogoni et al. 2013a, Prediction of PSD in nonisothermal antisolvent crystallization)

$$r = 0.5264 + 0.5983 * q - 6.4588 * 10^{-4} * T \quad (4)$$

It is possible to verify the dynamic of the salt consumption with respect to the operating conditions which are temperature and antisolvent flow rate in this case. For example, increasing antisolvent flow rate (q) favours crystal growth rate and appropriately the salt consumption. On the other hand increasing temperature has an adverse effect on crystal growth. Therefore, it is expected to have a smaller rate of salt reduction when the temperature is high. It should be noted that although the solubility of sodium chloride is almost independent of temperature, for the ternary system of water-sodium chloride-ethanol, temperature affects the hydrogen bonding properties of the solvents (Cogoni et al., 2013b, hydrogen bond interactions in isothermal and non-isothermal antisolvent crystallization processes) and as a result it influences crystal growth and the rate at which sodium chloride precipitates. However, the effect of antisolvent flow rate is more noticeable compared with temperature.

4. Results and discussion

In Figure 4 the results of the above model (Equations 3 and 4) are compared with the experimental data provided for nine different operating conditions. A quite good agreement is observed for all cases. However, the β parameter is not constant. In particular, while for high and medium flow rates the values are quite close (2.15 and 2.47), for low flow rates this value is rather different (3.6). This fact could be explained by considering that the dimension of the crystals, which affects the salt consumption, increases when the antisolvent flow rate decreases (Grosso et al., 2010 Stochastic formulation of CSD).

In order to use the model over the whole operating range, it is important to take into account the explicit dependence of parameter β on the antisolvent amount. In particular, the resulting equation that allows correlating β with the antisolvent flow rate is given as.

$$\beta = \frac{2.09}{1 - \exp(-1.24 * q)} \quad (5)$$

In Eq(5) the β parameter changes inversely with the amount of antisolvent flow rate. Therefore, as the antisolvent feed rate decreases β increases in order to compensate for the dimension of the crystals that changes for different antisolvent regime. The obtained global model has been also validated considering the flowrate and temperature trajectory reported in Figure 5. In the proposed run the antisolvent addition policy starts at high value of the flow in the operating range (3 ml/min) and it is reduced after 30 minutes to 2.2 ml/min. On the other hand the temperature of the reactor is kept constant at its lowest value for the first half an hour of the experiment and it is then increased to a higher value of 15.1°C and converges to this value after some small fluctuations. The results in terms of salt content in the reactor are reported in Figure 5. As can be observed at the beginning of the run, due to high antisolvent flow rate and low temperature, the rate of salt consumption is rather high and when the step changes are imposed to the system, rate of salt dissipation reduces, and after 350 minutes it reaches a plateau when the rate of salt that is deposited with respect to antisolvent added can be assumed to be negligible due to small affect that the antisolvent addition has on the equilibrium concentration when the volume of reactor contents is high. The agreement of the obtained results compared with the experimental data is quite good and the model is capable of predicting the system at different rates of salt consumptions and in the existence of fluctuation in both temperature and flow rate. This gives us the possibility to use the above model in online control and optimization applications, that is, using the model to estimate the real concentration to control the supersaturation to reach a desired value of crystal size, or to set up a dynamic optimization problem when the optimum trajectory of temperature and antisolvent flow rate are sought in order to minimize the amount of salt to achieve a specific crystal size distribution

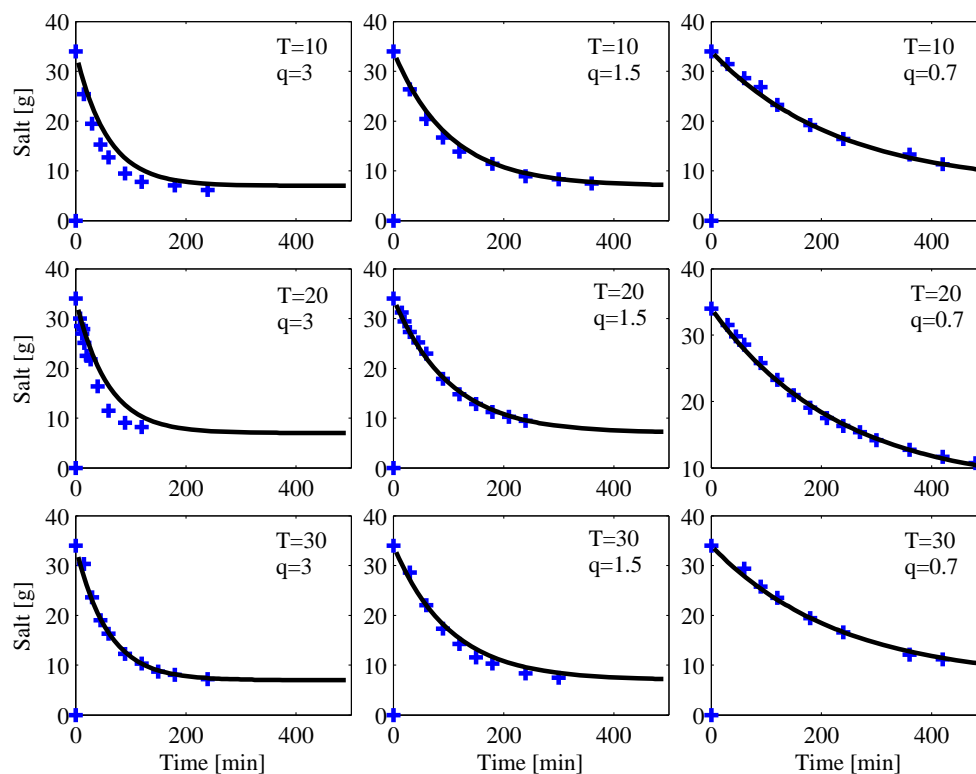


Figure 4: Comparison between the model and experimental values for the nine different operating conditions

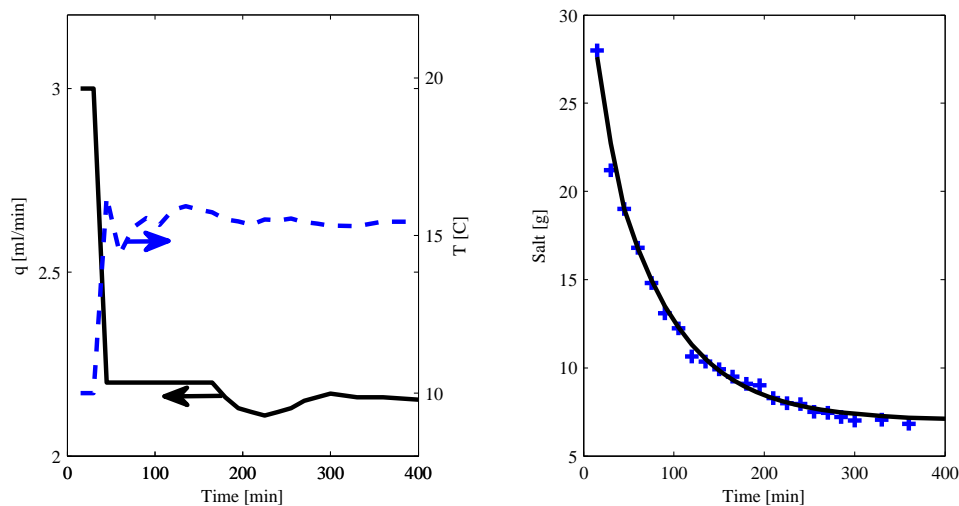


Figure 5: Antisolvent flowrate and temperature profile for the validation run and the comparison between the model and experimental values

5. Conclusions

An In-situ method for the on-line measurement of the salt concentration was developed. Crystallization of sodium chloride in water using ethanol as antisolvent was considered as a case study. The real concentration will be inferred by the simultaneous measurement of temperature, antisolvent mass fraction and electrical conductivity. A calibration test was performed at constant temperature and for different mass fraction of ethanol in order to find the limiting conductivity of the solutions at constant ethanol mass fraction. The locus of these points was tracked as an exponential model of concentration as a function of conductivity. Subsequently, a deterministic model was developed to characterize the dynamic of the salt consumption. It

was assumed that the reaction rate coefficient is proportional to the logistic equation from (Cogoni et al. 2013a, Prediction of PSD in nonisothermal antisolvent crystallization) which is multiplied by a parameter β correlated with antisolvent flow rate. Results of the above model were compared with the experimental data for typical operation profile for both antisolvent flow rate and temperature and a good agreement was observed between the model and the experimental data.

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