4. Experimental work

4.1. Fluidized bed experiments

4.1.1. Fluidized bed measurement equipment

The fluidized bed crystallization system, already used and discussed e.g. by [1, 4, 62, 101] is consists of a pump and two heat exchangers in addition to cell. The fluidized bed cell is shown in ***Fig. 4.1.***, and is made of acrylicglass. The crystallization system is assembled in the process of chemical engineering department's laboratory. The pump is a centrifugal pump (Iwaki magnet pump, model MD 30R-220N), the two heat exchangers were connected to two water baths, one (HAAKE N3, typ 001-5722) adjusted to keep the solution undersaturation in the vessel (heating) while the other (HAAKE F3, typ 002-0991) operates as a cooler to create the required supersaturation and undersaturation level in the growth and dissolution zone, each water bath is connected to a centrifugal pump.

4.1.2. Procedure

The experimental setup of the fluidized bed crystallization system is shown in ***Fig. 4.1..*** It consists of a pump and two heat exchangers in addition to a cell. The fluidized bed cell is made of acrylglas. The pump is a centrifugal pump. The two heat exchangers were connected to two water baths. One to keep the solution under-saturation in the vessel (heating). The second heat exchanger operates as a cooler or heater to create the required supersaturation or undersaturation level in the growth and dissolution zone, respectively.

A saturated solution of $NaCl/MgSO_4 \bullet 7H_2O$ is prepared according to the solubility data of Mullin [67]. The solution was prepared by dissolving the required amount of $NaCl/MgSO_4 \bullet 7H_2O$ in 7 liters of distilled water. The saturated solution is transferred to the reservoir of the crystallization system. The solution started circulation through the crystallization system. The temperatures of the two water baths were adjusted to keep the solution undersaturation in the reservoir (heating) and slightly supersaturated or undersaturated in the growth and dissolution zone (cooling/heating). Usually a temperature is decreased less than the saturation temperature to have the

solution in the metastable zone for the growth rate measurements. For dissolution rate measurements, a temperature higher than the saturation temperature is enough to create the required undersaturation. In case of growth rate measurements in dependence of an impurity concentration a carefully weighed amount of impurity is added to the solution.

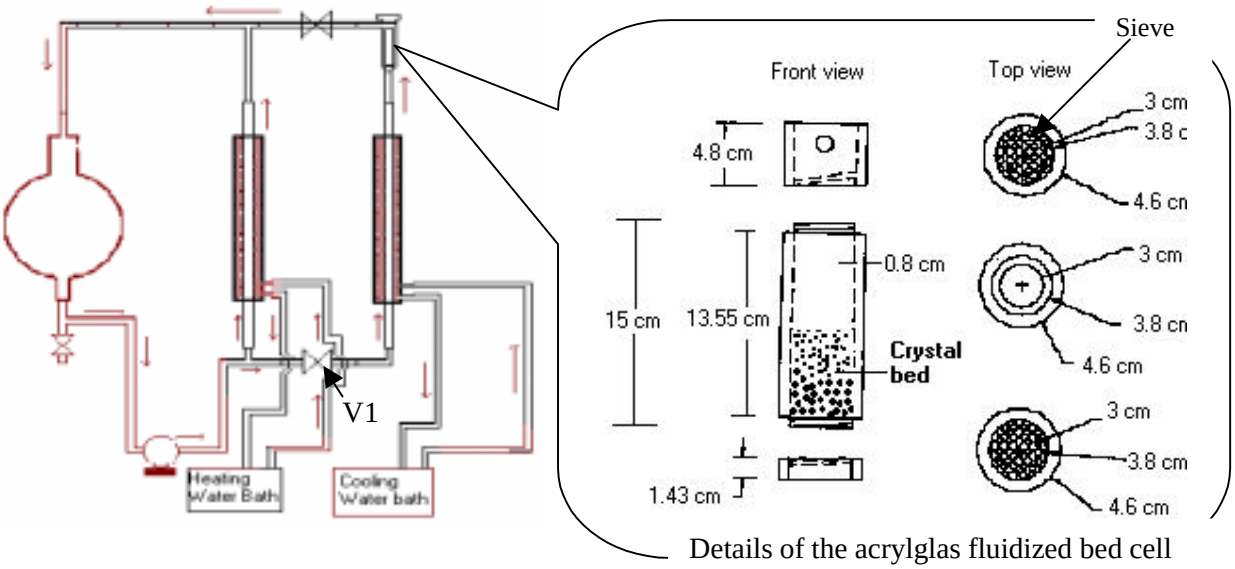

***Figure 4.1.**: Fluidized Bed Experimental Setup.*

With *NaCl* experiments the saturation temperature was 30°C the seed crystals were 315–250 μm and the initial weight for all runs was 5 g. These seeds were put into the cell. When the temperature of the solution reached the required temperature, the cell was fixed in its place. Adjusting the valve V1 in the system controlled the fluidization velocity. A stopwatch was used to evaluate the operating time for each run. At the end of the run, valve V1 was fully opened to keep the solution away from the cell then the cell content was filtered and washed with ethyl alcohol. The filtered crystals were dried at 50°C for 4 hours. After that, the crystals were cooled to ambient temperature and weight. The difference in weight of the crystals before and after the experiment is used in calculating the growth rate or the dissolution rate, respectively.

While, in the case of $MgSO_4 \bullet 7H_2O$ experiments the saturation temperature was 25°C, the seed crystals were obtained from sieve fractions with a mean size 1mm. In all runs the initial weight of seed crystals was 3 g. After 15 of growth minutes the crystals were washed with ethanol, dried at room temperature and weighed.

Changing the pH-value of the solution is done by addition of H_2SO_4 to obtain acidic solutions and *NaOH* to obtain alkaline solutions. In case of growth rate

measurements in dependence of impurity concentrations a carefully weighed amount of impurity is added to the solution.

Table 4.1.: *The operation conditions of NaCl solution in a fluidized bed crystallizer at a saturated temperature = 30℃.*

Condition	*Values*
Super/undersaturated temperature °C	1–7°C / 1–6°C, respectively
Impurity species (ppm)	
$CuSO_4 \bullet 5H_2O$	5, 10, 25
$K_4Fe(CN)_6 \bullet 3H_2O$	1, 10
$MgCl_2$	50, 100, 250
$PbCl_2$	0.5, 1, 10

Table 4.2.: *The operation conditions of $MgSO_4 \bullet 7H_2O$ solution in a fluidized bed crystallizer at a saturated temperature = 25℃.*

Condition	*Values*
Super/undersaturated temperature °C	0.2–1°C
pH value of the solution	2.5, 3.8, 7.7, 8.6
Impurity species (wt %)	
Borax ($Na_2B_4O_7 \bullet 10H_2O$)	0.5, 1, 2, 5
$FeSO_4 \bullet H_2O$	1, 2
K_2SO_4	2, 4
KCl	2, 5
KH_2SO_4	1, 3
$MgCl_2$	1, 2
Na_2SO_4	2, 5
NaCl	2, 5
$NiSO_4 \bullet H_2O$	1, 2

4.2. Electrophoretic-mobility measurements

Electrophoretic-mobility measurements were done by the Laser-Doppler electrophoresis technique [102]. The zetasizer 3000 with the AZ4 standard cell was used for measuring electrophoretic-mobility. The zetasizer 3000 is consisted of, two coherent laser beams of red light produced by splitting of a low power He-Ne laser are focused and made to intersect within the quartz capillary cell holding the particle suspension at a point of zero convective flow. As a result, a pattern of interference fringes is formed, and the particles move across the fringes under the influence of the applied electric field scatter light. The of the scattered light varies with a frequency that is related to the velocity of the particles. A fast photomultiplier together with a digital correlator is used to analyse the signals, and the distribution of particle velocity (electrophoretic-mobility) and/or distribution of *zeta potential* is thus determined. The sign of the zeta potential is determined by referencing the observed Doppler frequency of the light scattered by the particles moving through the fringes to the modulation frequency applied to one of the laser beams.

Fig. 4.2. presents a schematic diagram of the AZ4 standard cell used in the present study. This cell consists of a 4 mm diameter quartz capillary. The platinum electrodes are in compartments at each end of the cell. A semipermeable membrane separates the electrodes from the suspension sample to prevent the contamination of the electrodes by the sample. The electrode chambers are filled with an electrolyte which is at least conducting as the sample itself. Polarization of the electrodes is prevented by the application of a periodically reversed field.

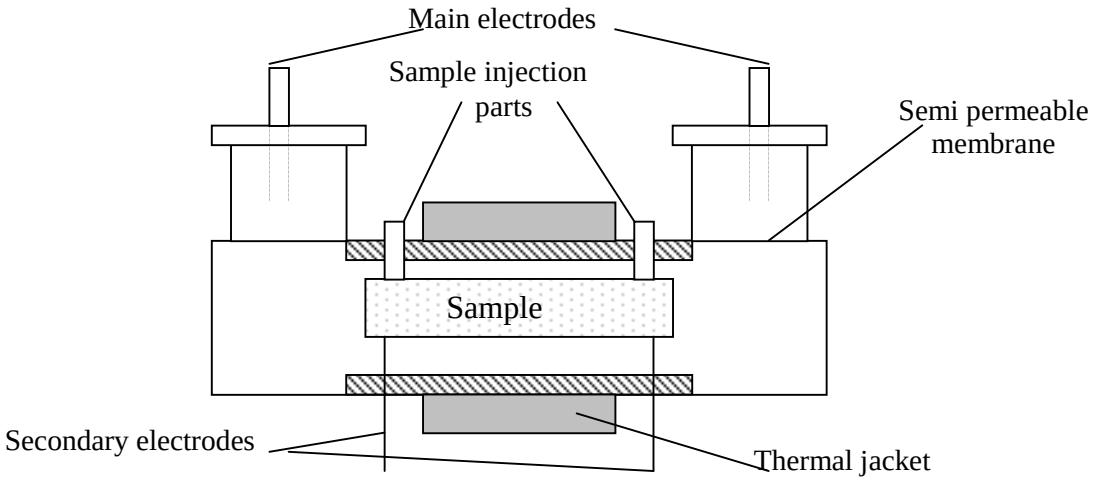

Figure 4.2.*: Schematic diagram of the capillary electrophoresis cell for the zetasizer 3000.*

Of course a zeta potential/electrophoretic-mobility measurement in a saturated solution is impossible because the double layer is collapsed, the high conductivity of saturated solutions causes some measurement problems, and the zeta potential does not exist, even through a surface charge may still be present. In order to describe the electrokinetic behaviour of the soluble-salt particles, the electrophoretic-mobility measurement of the $MgSO_4 \bullet 7H_2O$ crystals < 80 μm were made after diluting the saturated solution by ethanol (45 mole % ethanol in solvent). Importantly, however, these measurements should give a relative indication in the sign of the surface charge of the $MgSO_4 \bullet 7H_2O$ crystals in their saturated solution.

4.2.1. Procedure

The soluble salts were sized and the 80 mesh fraction was used in this study for electrophoretic-mobility measurements. The electrophoretic-mobility of the $MgSO_4 \bullet 7H_2O$ was measured in the following steps:

1. Prepaire a saturated solution of $MgSO_4 \bullet 7H_2O$ in aqueous ethanol solution (45 mole % in solvent).
2. 0.5 g of well defined crystals of a sieve cut, < 80 μm, of $MgSO_4 \bullet 7H_2O$ were added to the saturated solution.
3. The suspension salt crystals was stirred for 1-2 minutes and then quickly injected into the cell of the electrophoretic-mobility measured.
4. Each measurement required approximately 4-10 minutes, depending on the impurities added to the pure solution.

Its should be mentioned that:

1. The salt particles must be suspensioned in the saturated solution, otherwise there is no significant effect to measure the electrophoretic mobility/*zeta potential*.
2. The concentrations of impurities added to the solution were 10-20 wt %, at low impurities concentration there was no change in the values of the electrophoretic-mobility measured for impure solution comparsion with pure solution.
3. Great care is taken to avoid injection of air bubbles into the cell.
4. The experiment was repeated at least 3 times for each impurity under the same conditions to determine the reproducibility of the measurements.