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An insight into interparticle forces and filterability of potassium sulphate crystals precipitated with ethanol and acetone

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Abstract

Solvent effects on formation of secondary crystals, in semibatch operating precipitation, were studied with potassium sulphate using acetone and ethanol as an anti-solvent. Zeta potential measurements were carried out to investigate the attractive or repulsive interaction of primary crystals forming firstly via primary nucleation and crystal growth by varying the pH of the solution. Particle size characterization were conducted using optical microscopy and image analysis. In addition to crystal size investigation to characterize the end product, the filterability of obtained crystals was determined using a Nutsche pressure filter. The obtained results showed that acetone yielded smaller crystal sizes and lower filterability than ethanol with the used precipitant feed rates. The isoelectric point for the acetone solution was obtained at a pH range of 5.5 to 6.5, whereas for the ethanol solution the isoelectric point was expected to be around a pH lower than 3.5 based on extrapolation. The zeta potential values varied less as a function of pH in acetone solutions than in ethanol solutions.

Keywords: precipitation, filterability, potassium sulphate, zeta potential, image analysis

1. Introduction

Concerning the operation of precipitation processes the mixing and feeding conditions of a precipitant or a reactant (or several) influence greatly on the properties of the crystalline product. Therefore, the fluid dynamics, concentrations in feeding flows and rheology of the solid-liquid suspension are crucial issues for precipitation processes. This is usually the case both in semibatch operating reactive crystallization and salting-out precipitation. In the former case the reaction yields typically a sparingly soluble solid product whereas in the latter case a precipitant is used to decrease the solubility of the crystallizing solute usually under isothermal conditions. The mixing conditions at micro, meso and macro scale can affect significantly on precipitation. The fluid dynamics of precipitation has been investigated widely (Mersmann and Rennie, Baldyga and Jasinska, Vicum et al., Baldyga and Orciuch, Sathyamoorthy et al.). Mumtaz and Hounslow studied the influence of fluid dynamics on aggregation as a crystal size enlargement mechanism. The present work focuses on the investigation of solution composition impacts on the crystal characteristics in out-salting precipitation using two anti-solvents as precipitants.

Precipitation is a complicated unit operation to model. The precipitation kinetics include the primary nucleation rate of primary crystals, the attrition nucleation rate due to crystal breakages, the crystal growth rate of primary crystals, and the rate of secondary growth processes, such as aggregation or agglomeration. In this work the term ‘secondary crystals’ are used for aggregates and agglomerates. The characterization of secondary crystals is based on optical microscope observations. Secondary crystals formed by primary crystals held weakly together are classified as aggregates and crystals cemented firmly together by solid crystalline bridges are agglomerates. The formation of secondary crystals may decrease crystal purity if the secondary crystals contain inclusions or occlusions where the mother liquor can be trapped in. On the other hand the secondary growth process may also enhance the solid-liquid separation (Yang et al.). The crystals to first appear are on the micrometer or even nanometer size range. The behavior of the suspended particles in this size range is typically governed by the interfacial forces in such a manner that the fine particles are affected by the electrical attractive or repulsive forces of the double layer surrounding the particles. Therefore, the final product particles are mainly secondary crystals formed by aggregation or agglomeration of small primary ones. The principal force affecting secondary crystals in solid-liquid suspensions is gravity. Supersaturated conditions may cause harder bridges between particles and therefore, harder structures of the secondary crystals. When secondary crystals are formed, an increase in the roughness of the crystal surface and in the specific surface area of crystals may also make dewatering, filter cake washing and thermal drying more difficult.

The zeta potential is widely utilized to investigate the stability of a solid-liquid suspension containing submicron sized colloids (Ketelson et al.) and as a tool to choose an appropriate stabilizer (Talens-Alesson). Furthermore, the zeta potential is a tool which makes it possible to determine a favorable solution composition as a pre-treatment for several separation processes containing small particles, such as sedimentation (Gustafsson et al.), filtration (Wakeman and Tarleton) and precipitation. According to the DLVO theory (Mersmann and Braun) the stability of colloidal systems can be expressed by the sum of the electrical double layer repulsive force and van der Waals attractive force when the particles approach each other. To adhere to each other, the particles should have sufficiently high collision energy to exceed the energy barrier and, therefore, overcome the repulsive force not allowing particles to come sufficiently close to each other. Impurities may change the double layer conditions at the solid surface. The zeta potential is the electrical potential between the bulk solution and the shear plane of the particle. The value of the zeta potential indicates if interaction forces between colloids are repulsive or attractive. At the isoelectric point (IEP) the zeta potential is equal to zero; the stability of the suspension is at its lowest and formation of secondary particles via agglomeration or aggregation can be expected to occur. In electrolyte solutions it is possible to influence the zeta potential by varying the pH. For a particle the zeta potential is a parameter which can be deduced from the electrophoretic mobility which depends on pH, ionic strength, viscosity, temperature and dielectric constant of the suspending liquid.

The present work focuses to study the influence of chemical composition on a semibatch salting-out process and downstream processing, on the filterability of the precipitate. The solvent effects on the formation of secondary crystals in precipitation and the filterability of the obtained crystals were studied with salting-out precipitation of potassium sulphate using ethanol and acetone as anti-solvents. In many applications the filterability of the crystals is a criterion used to define how good the crystals obtained by crystallization are, i.e. how trouble-free the solid-liquid separation is and what is the required filtration time. This comes from the entire integrated crystallization process where crystallization as a unit operation is followed by solid-liquid separation in downstream processing. Mydlarz and Jones and Mullin et al. used aqueous acetone in out-salting of potassium sulphate from aqueous solution. Furthermore, Mydlarz and Jones investigated the filterability of crystals obtained by continuous cooling crystallization and salting-out precipitation. They showed that diluted precipitant enhanced solid-liquid separation. The goal of the present work was to compare out-salting processes of potassium sulphate with two organic precipitants having different chemical character in solutions having different pHs. pH was decreased by adding sulphuric acid into the solution. The present work consists of results from zeta potential measurements based on electrophoretic mobility, particle size and shape characterization results using optical microscopy and the filterability results of crystals employing constant pressure filtration. The hypothesis of the present work was based on the assumption that higher agglomeration tendency and a lower filterability coefficient can be obtained when precipitation conditions are close to the isoelectric point (IEP, zeta potential approaches zero value).

2. Experimental Procedures and Results

2.1. Materials

The solubility data of potassium sulphate in the studied solutions containing water and acetone or ethanol were taken from literature according to the Solubility of inorganic and organic compounds and Mydlarz and Jones. The solubility data are shown in Fig. 1. Potassium sulphate supplied by J.T. Baker (min. purity 99 %), ethanol supplied by Alko (Absolute Ethanol, min. purity of 99%) and acetone supplied by Merck (pro analysi, min. purity 98 %) were used in the experiments. pH was decreased using sulphuric acid (95-97 % H_2SO_4, Merck, pro analysi) diluted with deionized water to a concentration of 2 vol-%. The solubility of potassium sulphate in the solutions at lower pH was determined experimentally and the obtained results showed that the acid used does not significantly change the thermodynamics of the studied system. In aqueous electrolyte systems the polarity of the solvent may affect the interaction in binary solvent systems. Marcus gives a normalized solvatochromic parameter (references: maximal polarity water $E_T^N = 1.00$ and minimal polarity tetramethylsilane $E_T^N = 0$) value for acetone $E_T^N = 0.355$, and for ethanol, $E_T^N = 0.654$, which shows that acetone is a less polar solvent than ethanol.

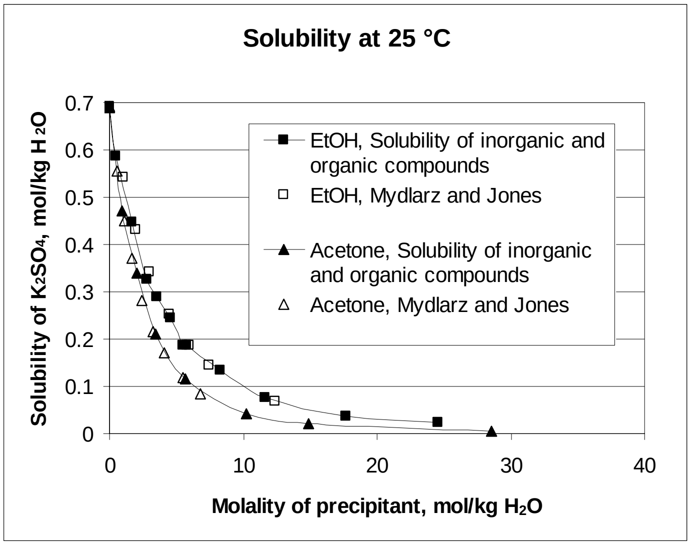


Figure 1: Solubility of potassium sulphate in aqueous acetone and ethanol solutions.

2.2. Crystallizer

The employed crystallizer was a jacketed 1-liter glass reactor. An Ismatec sa MS 4 reglo peristaltic pump was used as a feed pump and the diameter of the feed tube was 1 mm. The four-baffled crystallizer had a U-shaped bottom and an inner diameter of 100 mm. The employed precipitation system is shown schematically in Fig. 2. A straight three-bladed impeller having a diameter of 48 mm was used as the stirrer at a rotation speed of 600 rpm. The salting-out experiments listed in Table 1 were carried out under isothermal conditions at 25 °C. The feeding position of the anti-solvent and agitation intensity were fixed. The feeding point of anti-solvent was located as close as possible to the mixer. The batch time was changed by altering the constant feed rate of the anti-solvent. The initial aqueous solution contained potassium sulphate 10.7 w-% and was saturated at 25 °C (82.5 g potassium sulphate dissolved in 687.5 g water, the intercept of the y-axis in Fig. 1). The quantity of acetone was chosen in such a way that the crystal yield related to anti-solvent consumption was maximized. With acetone the final composition was 24.7 w-% acetone (230 g, pumping time 73-140 min), 73.9 w-% water and 1.4 w-% potassium sulphate. The same anti-solvent concentration on mole basis both with acetone and EtOH was used, and thus, the total amount of 180 g EtOH was pumped into the solution (pumping time 62-110 min). Therefore, the composition of the ethanol solution was 20.4 w-% EtOH, 77.8 w-% water and 1.9 w-% potassium sulphate. It should be noted that based on the above solution compositions for both anti-solvent systems the suspension density was slightly different during the course of precipitation. Also, the superaturation levels are expected to be different in these two anti-solvent systems with the same feed rate of anti-solvents, as can be seen from the solubility curves in Fig. 1.

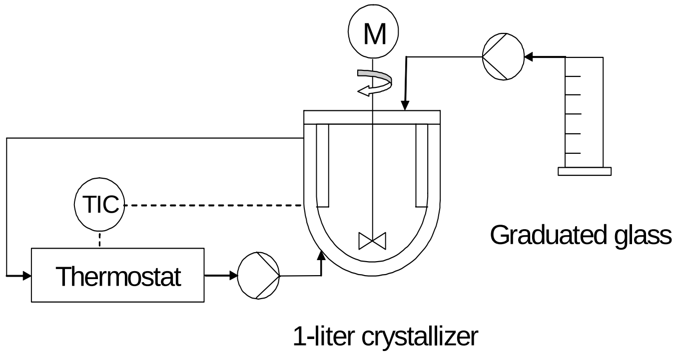


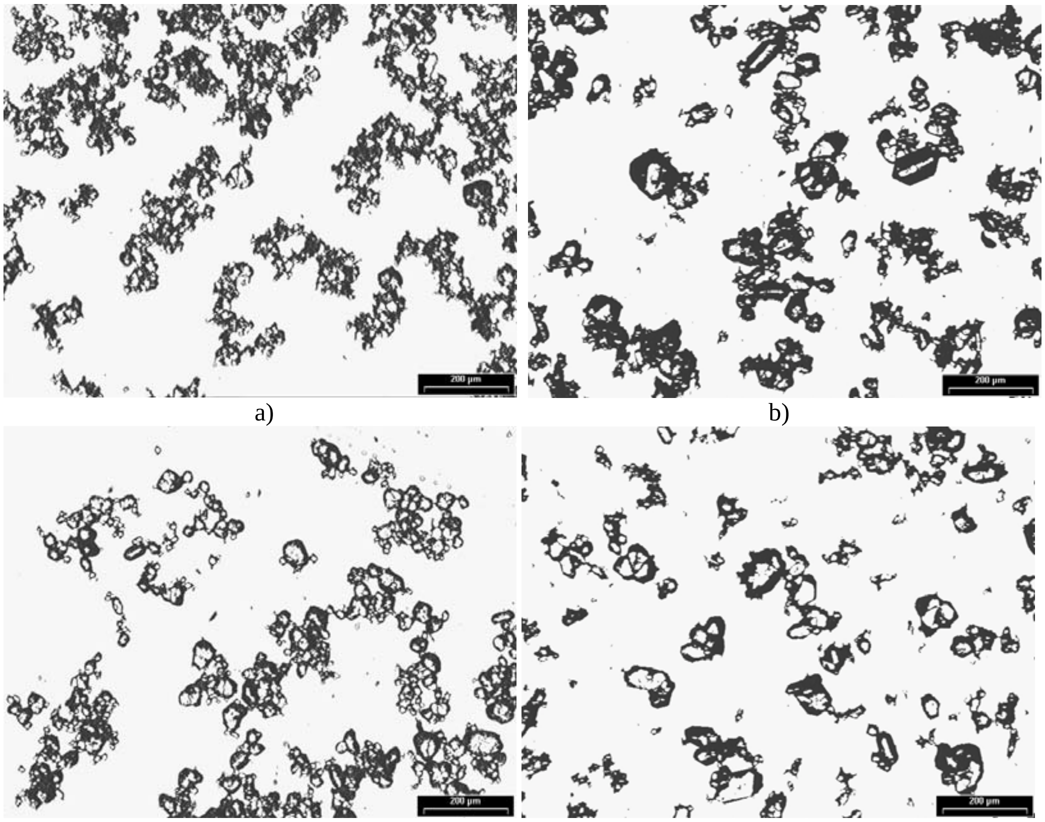
Figure 2: Experimental set-up.

Table 1. Salting-out experiments with acetone and ethanol as precipitant.

Acetone		Ethanol	
pH	Feed rate, mL/min	pH	Feed rate, mL/min
3.7	2.09, 3.17, 4.00	3.7	2.04, 2.86, 3.70
3.84	3.17	4.33	2.04, 2.86, 3.70
4.33	2.09, 3.17, 4.00	6.2	2.04, 2.86, 3.70
5.93	2.09, 3.17, 4.00		
6.2	2.09, 3.17, 4.00		

2.3. Image analysis

The particle size, the specific equivalent circle diameter, $\mathrm{ECD} = 2(A/p)^{1/2}$, of the detected particles was measured to determine mean crystal size using an optical microscope Olympus BHS, a Hamamatsu C4200 video camera, a C2400 camera unit and image analysis software analySIS® 3.0. With a büchner funnel filtered and dried crystals were used in image analysis. All the size distributions consisted of a minimum of 600 particles. The micrographs of the crystals obtained for the two studied precipitants are shown in Fig. 3.



a) b)

c) d)

Figure 3: Micrographs of out-salted potassium sulphate crystals at pH 6.2 with various precipitant flow rates: a) acetone 4.24 mL/min, b) ethanol 3.82 mL/min, c) acetone 2.18 mL/min, and d) ethanol 1.99 mL/min). Scale bar 200 µm.

2.4. Zeta potential based on electrophoretic mobility

Zeta potential measurements were carried out to study the interaction between crystals. The employed zeta potential analyzer was a Coulter Delsa 440. The measuring method, Electrophoretic Light Scattering (ELS), was based on electrophoresis where particles are characterized by their mobility in an electric field and laser doppler velocimetry. The analyzer is provided also with a conductivity meter. The solid-liquid suspension samples were taken after precipitation. At the studied pH ranges, the obtained conductivities of the acetone solutions varied between 7.4-7.9 mS/cm, and for ethanol solutions the range was 11-12.2 mS/cm. The zeta potential, ζ, is defined as follows:

$$\varsigma = 4\pi\mu U / \varepsilon \tag{1}$$

The electrophoresis mobility can be defined with the aid of the terminal velocity of the particles, ν, and the applied electronic field, E:

$$U = \nu / E \tag{2}$$

The laser doppler velocimetry allows the measuring of the speed of the particles by analyzing the doppler shifts of the scattered laser light. Determining electrophoretic mobility requires also data on the solution refractive index. The experimentally obtained values for acetone and ethanol solutions at 25 °C were 1.348 and 1.345, respectively.

The dielectric constant depends on the interatomic and intermolecular attractions and it shows the efficiency of a solvent to separate the electrolytes into ions (Jouyan et al.). A relationship between the dielectric constant, temperature and the anti-solvent content was taken from Åkerlöf's experimental data and the fitted data are shown in Table 2. Although the solution contains potassium sulphate as a solute, it can be assumed that there is such a high quantity of free solvent molecules that the solute effect can be ignored for a solute concentration lower than 3 molal (Barata and Serrano). From Åkerlöf's data obtained the dielectric constant value at 25 °C for acetone solution was 63.8 F/m, and for ethanol solution 66.5 F/m. The dynamic viscosities were determined using a Schott-Geräte capillary viscosimeter 525 10 / I with an internal diameter 0.63 mm and capillary constant 0.01013 mm^2/s^2. The liquid density was determined by weighing 25 mL of saturated solution. The filtrate density of the ethanol solution was 963.6 kg/m^3 and the filtrate viscosity was 1.79 mPa s. For a final acetone concentration of 23 % by weight the averaged filtrate density was 961 kg/m^3 and viscosity 1.36 mPa s.

The isoelectric point was determined by measuring the zeta potential at various pH values for both anti-solvent systems. When adding 180 g ethanol in out-salting, the IEP appeared to be below 3.7 by extrapolation and for the acetone solution it was at a pH range of 5.5-6.5. The obtained zeta potential results showed that the values for acetone solutions varied between -12 and +5 mV, whereas for ethanol solutions the range was -36 to -18 mV (Fig. 4).

The neutral aqueous potassium sulphate solution in the presence of acetone had a zeta potential close to zero whereas in ethanol solution the averaged zeta potential value was approximately -33 mV. In the presence of ethanol, the zeta potential was proportional to the conductivity whereas the conductivity of acetone solutions varied only slightly, as discussed above in this section. Furthermore, precipitates from ethanol solutions had a greater equivalent circle diameter (ECD) the lower the pH, as shown in Fig. 4.

Table 2. Dielectric constant expressions of aqueous acetone and ethanol solutions at 25 °C (fitted from experimental data published by Åkerlöf).

Anti-solvent	Dielectric constant
Acetone	ε [F/m] = -0.6082 × c [w-% acetone]+78.825
EtOH	ε [F/m] = -0.5676 × c [w-% EtOH]+78.048

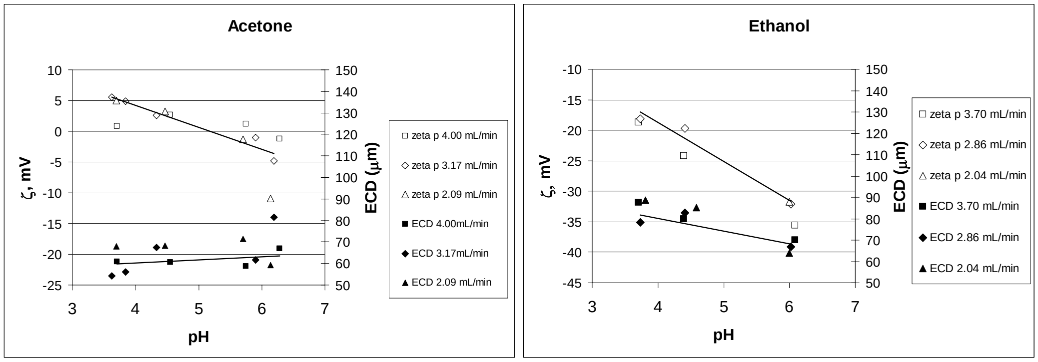


Figure 4: Measured zeta potentials and the equivalent circle diameter of potassium sulphate precipitated with acetone and ethanol with various flow rates of precipitant.

2.5. Nutsche pressure filter

A Nutsche pressure filter of laboratory scale with a filtration area of 19.6 cm^2 and volume 350 mL was used in the filtration experiments. The constant filtering pressure was 1 bar using pressurized nitrogen. The flow rate of the filtrate was logged over time with a scale connected to a PC provided with data acquisition software. Filtration parameters are determined from the modified expression for constant pressure filtration (Wakeman and Tarleton):

$$\frac{t-t_o}{V-V_o} = \frac{F_k}{2A^2}\left(V+V_o\right) + \frac{\mu R}{A\Delta p} \tag{3}$$

The latter term on the right hand side represents the influence of the filter medium on the filterability. For a selected filter medium the filterability coefficient of the solid material can be used for scaling-up of constant pressure filtration and is defined according to Wakeman and Tarleton as:

$$F_k = \frac{\alpha_{av} c \mu}{\Delta p} \tag{4}$$

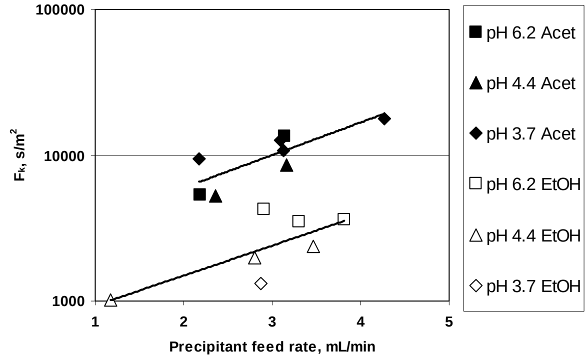


Figure 6: Filterability coefficient of potassium sulphate out-salted with acetone and ethanol.

The obtained values of the filterability coefficients for solutions with various pHs as a function of the flow rate of anti-solvent are shown in Fig. 5. Crystals out-salted with ethanol had better filterability than those out-salted with acetone. The main reason can be explained by the larger primary crystal size obtained for ethanol solution.

3. Conclusion and Discussion

The main subject of the present work was to investigate salting out precipitation using two precipitants and characteristics of obtained crystals based on image analysis and filterability study, and zeta potential study of a solid-liquid suspension. The chosen compound was potassium sulphate which was precipitated from aqueous solutions with ethanol and acetone as studied anti-solvents. Based on the experimental results obtained, it seems that the feed rate has a greater influence on the primary particle size than the pH. As the size of the primary particles change with the feed rate, so does the zeta potential.

According to the obtained zeta potential results, it can be expected that in acetone solutions the primary crystals tend to form secondary crystals more easily. The external appearance of aggregates salted-out with acetone did not increase the permeability of the crystal cake to such an extent that the filterability with acetone exceeded the cake permeability of the crystal cake obtained using ethanol as the precipitant. Also greater equivalent circle diameter values when using ethanol prove that the crystal size ranges were different. The primary crystals obtained with acetone remained small causing a higher specific crystal surface in the filter cake in spite of varying precipitation conditions. The main conclusion drawn was that out-salting with ethanol yielded crystals more easy to filter than acetone.

4. Nomenclature

A	area of the filter, m^2
c	initial solids concentration of the suspension, kg/m^3
E	electronic field, V/cm
F_k	filterability coefficient, s/m^2
Δp	pressure difference, mPa
R	medium resistance, 1/m
t	time, s
U	electrophoresis mobility, $m^2/(V\ s)$
V	cumulative volume of the filtrate discharging from the filter, m^3
v	terminal velocity of the particles, m/s
α_{av}	average cake resistance, m/kg
ε	dielectric constant, F/m
μ	dynamic viscosity, Pa s

Subscripts

o	initial

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