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The mechanism of particle formation during homogeneous precipitation of zinc sulfide

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Abstract: Monodisperse zinc sulfide particles were prepared by homogeneous precipitation from zinc sulfate solutions. Particle size could be adjusted in the range of 1 to 5 microns by changing the viscosity of the reaction medium. From electron micrographs of particles prepared in high viscosity media subparticles up to 50 nm in diameter could be observed. From these results it was concluded that particle growth took place predominantly by Brownian coagulation.

Furthermore, it was established that stirring the reactor content during the initial phase of particle formation alone did not influence particle size, nor did it promote coagulation of micron-sized spheres. We were able to prepare this material in amounts up to 2 kg of solid material from a reactor with a working volume of 36 l.

Key words: Zinc sulfide – homogeneous precipitation – thioacetamide – Brownian coagulation – induction period

1. Introduction

Zinc sulfide is a highly crystalline material. Nevertheless, it can be precipitated as spheres with a narrow size distribution. They are formed if thioacetamide is hydrolized, thus generating hydrogen sulfide, in aqueous solutions of zinc salts. However, in order to obtain monodisperse and nonagglomerated particles the final suspension density must be less than one per mille.

Wilhelmy and Matijević developed a two-step proces [1]. In the first step, they grew particles with a diameter less than 80 nm. These acted as nuclei in a second reaction where particles above 1 μm were obtained. From x-ray data, the authors showed these spherical particles to be highly crystalline. They were not able to explain these observations nor did they find any evidence for a substructure.

Wiliams, Yocom, and Stofko prepared zinc sulfide from aqueous solutions of zinc sulfate and thioacetamide in a one-step process [2]. Only under some strict conditions did they obtain spheres. The temperature distribution in the reaction vessel had to be very uniform and, in order to avoid aggregation, stirring of the reaction medium was not allowed. These authors did find some evidence for a substructure. From an x-ray analysis they calculated a crystallite size of about 12 nm and the spheres shown in their electron micrographs had a "tangled fibrous appearance".

Until recently, the formation of monodisperse particles was explained by a mechanism proposed by LaMer and Dinegar [3, 4]. A few years ago an alternative model to explain the formation of uniform particles has been published [5–7]. Nucleation now is not restricted to a short period in the beginning of the process, but does occur during a much larger time span. These nuclei grow until they reach a critical size range, usually on the order of 50 nm or less. From that moment on attractive Van der Waals forces are stronger than the repulsive electro-static ones and agglomeration results. According to this model, growth of particles in the 1-μm region proceeds predominantly by this agglomerative mechanism.

We were interested to find a way to produce these spheres at a higher suspension density.

Handling higher concentrations is hampered by the fact that stirring during the reaction is not allowed if aggregation of micron-sized particles is to be prevented.

2. Materials and methods

Materials

All materials in the laboratory-scale experiments were p.a. grade and were used as received. The Zn^{2+} source was $ZnSO_4 \cdot 7H_2O$ end was obtained from Merck as were thioacetamide and sulfuric acid (95–97%). Glycerine was from Brocacef.

In the pilot-plant scale experiments the Zn^{2+} source was a 1.7 molar technical grade $ZnSO_4$ solution. Technical grade thioacetamide was obtained from Courtaulds Chemicals. All other materials were the same as in the laboratory-scale experiments.

Apparatus

Laboratory-scale experiments were performed in a five-necked thermo-statted reactor of Pyrex glas at $T = 80\,^{\circ}C$. A 0.5-liter reactor was used during the experiments. It was equipped with a three-blade propellor with a glass-mantled shaft. Smaller vessels were not used because they would promote a significant loss of particles to the reactor walls. A pH electrode was used to determine the pH of the solution as a function of reactor time.

Pilot plant-scale experiments were performed in a 50-l reactor of Duran glass with a working volume of 36 l. A six-blade turbine impellar was used and the reactor temperature was controlled by a PID controller at a setpoint of 80 °C.

Laboratory – scale procedure

Thioacetamide was dissolved in 250 ml of the reaction medium (water or water/glycerine mixtures). Zinc sulfate was dissolved in 250 ml of 0.15 molar sulfuric acid. In order to facilitate complete dissolution and to avoid thermal gradients in the reactor the temperature of these solutions was raised to 80 °C. The resulting solutions were added to the pre-heated reactor under strong agitation. After the reaction a saturated polyvinylalcohol solution was added to the dispersion and the zinc sulfide particles were separated from the mother liquid by filtration (pore diameter 0.17 μm). Subsequently, the product particles were washed with demineralized water.

Pilot plant – scale procedure

Thioacetamide (21.75 mol) was dissolved in 30 l of reaction medium in an agitated pre-heated reactor. The second reactant solution was prepared by adding 5.4 mol of sulfuric acid to 6.35 l of a 1.7 molar zinc sulfate solution. These liquids were subsequently mixed at the reaction temperature. After 50 min the TAA-hydrolysis reaction was quenched by injection of cold demineralized water ($T = 18\,^{\circ}C$). The precipitate was subsequently separated from the mother liquid by filtration over a Buchner filter 30 cm. in diameter. Afterwards, the product particles were washed four times with 2 l of demineralized water and dried under vacuum at 40 °C. In this way, up to 2 kg of solid material could be obtained.

Particle characterization

The particle size distribution of the obtained samples was determined by forward light scattering, or Fraunhofer diffraction. The filtered and washed product powders were redispersed in water and subjected to ultrasonics for 1 h. The measurements were performed with a Coulter LS130. Particle characteristics were visualized by scanning electron microscopy (JEOL JSM 80A) as described previously [8].

3. Results and discussion

All preparations of zinc sulfide were carried out at a temperature of 80 °C and with $[ZnSO_4] = 0.0833$ mol/l, $[H_2SO_4] = 0.15$ mol/l and $[TAA] = 0.1667$ mol/l. Initially, we took care that during the entire reaction period the content of the reactor was not stirred. Currents in the reaction medium promote coagulation resulting in agglomerated products, as already pointed out by previous authors [1, 2].

Figure 1 shows the diameter of zinc sulfide spheres, obtained from SEM micrographs, as a

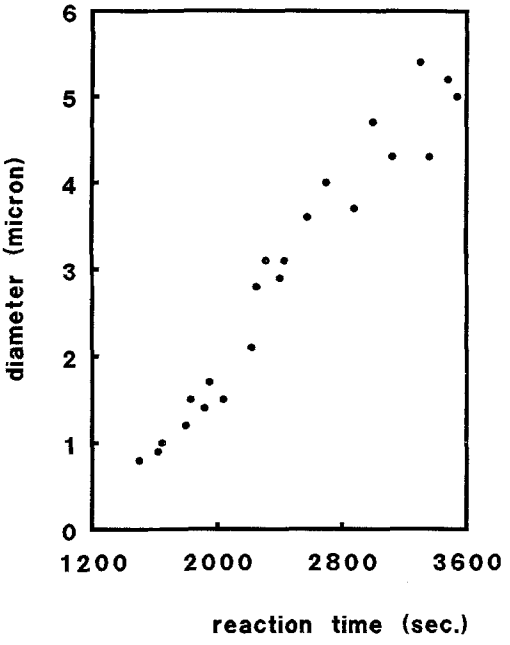

Fig. 1. Diameter of ZnS spheres as a function of reaction time at $T = 80\,^{\circ}C$

function of reaction time. In the first 1200 s the solution remained clear, although decomposition of thioacetamide did occur in this period, and the hydrogen sulfide thus released definitely reacted with the zinc ions in solution. During this induction period either no particles were formed or their diameter was smaller than 0.2 μm.

We observed that stirring during this induction period did not influence the particle formation mechanism. This is shown in Table 1 which gives the induction time at several values of the stirring rate. At that moment the stirrer was removed from the solution and the reaction was allowed to proceed in the usual way. The diameter of the spheres after a reaction time of 3600 s (including the induction period) is given in the last column of the table. Therefore, in all further experiments the reactor content was stirred vigorously during the induction period. This is a very important point if the reaction has to be carried out in pilot-plant-scale reactors. Such vessels cannot be operated without any stirring because of heat transfer problems. Moreover, the resulting convective currents are known to promote coagulation as well.

Table 1. Influence of the stirring rate in the laboratory – scale reactor on particle formation characteristics.

Stirring rate (r.p.m.)	Induction time (s)	Diameter (μm)
0	1620	5.0
120	1560	5.2
350	1500	4.8
480	1500	5.3
600	1440	5.1

One of the main objectives was to adjust particle size in the range of 1–5 μm. By varying temperature and concentrations of the reactants, we were not able to prepare monosized spheres with a diameter well below 5 μm at constant conversion. Usually, polydispersed and/or agglomerated particles were obtained. It is known that the size of silicon spheres, obtained from silicon alkoxides, can be adjusted by varying the ionic strength of the reaction medium [5–7]. In this case particle formation takes place by Brownian coagulation. An excess of electrolyte partially screens the charge on the spheres which results in a net attractive force. The coagulation rate increases and consequently larger particles are formed.

If this mechanism applies to the formation of ZnS particles, smaller spheres can be obtained if Brownian coagulation is retarded. This can be achieved by increasing the viscosity of the liquid phase by addition of glycerine. This did not give rise to problems as far as the dissolution of $ZnSO_4$ is concerned and the solubility of thioacetamide in water/glycerine mixtures is even better than in pure water. The results of these experiments are shown in Fig. 2. Here, the diameter of the ZnS spheres, as obtained from SEM micrographs, is given as a function of the viscosity of the liquid phase relative to the viscosity of pure water (μ/μ_0) at the reaction temperature of 80 °C.

Obviously, the results are fully consistent with a coagulative model for particle growth, as already reported by Celikkaya and Akinc [9]. In a reaction medium with a high viscosity the tendency for primary particles to coagulate is lower due to a reduced diffusion coefficient. Therefore, it is to be expected that the size of these primary particles is larger when prepared in high viscosity media because their growth period is longer. If they are large enough, they should be visible on electron micrographs. In the literature the substructure of ZnS spheres is hardly mentioned. Only Williams

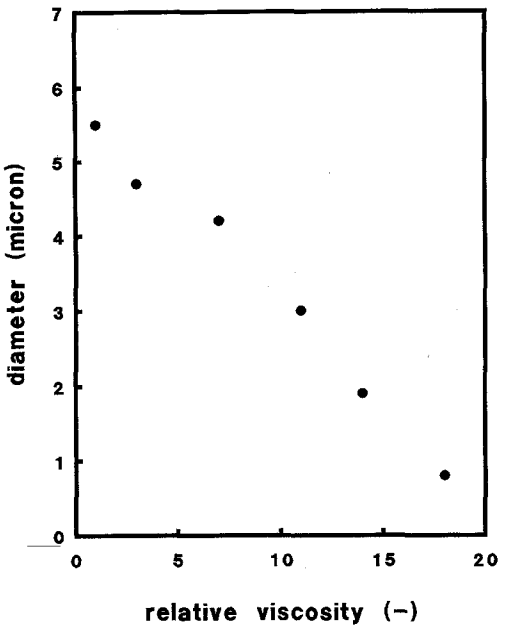

Fig. 2. Influence of the viscosity of the continuous phase on the diameter of ZnS spheres after a reaction time of 60 min

et al. reported that their particles had a fibrillous appearance [2].

In Fig. 3 is shown an electron micrograph of particles prepared in water/glycerine mixtures with a relative viscosity at 80 °C of 14 (at T = 20 °C this ratio is 80). Obviously, subparticles af about 50 nm can be observed. It is clear from this micrograph that packing of the primary particles is not random because they are arranged in strings of 7 to 10 units. Particles obtained in media with a lower viscosity do not show this substructure as clearly, but also in that case, fibrillous structures can be observed.

4. Conclusions

From the results presented in this paper, it can be concluded that particle formation during homogeneous precipitation of zinc sulfide takes place by Brownian coagulation of primary particles of 50 nm or less. The diameter of the final spheres can be reduced at constant conversion by increasing the viscosity of the reaction medium. In order to avoid coagulation of these larger particles no stirring is performed during their formation, but stirring during the induction period does not effect the resulting product. If the reaction is carried out in this way, the results of experiments in the 0.5 l and 36 l reactors match completely.

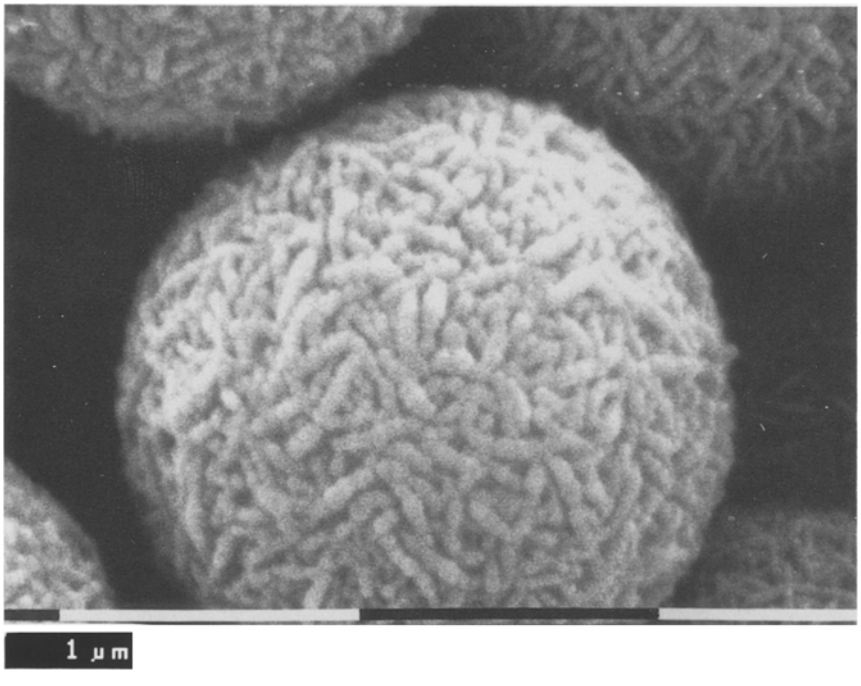

Fig. 3. Substructure of ZnS spheres at $\mu/\mu_0 = 14$

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