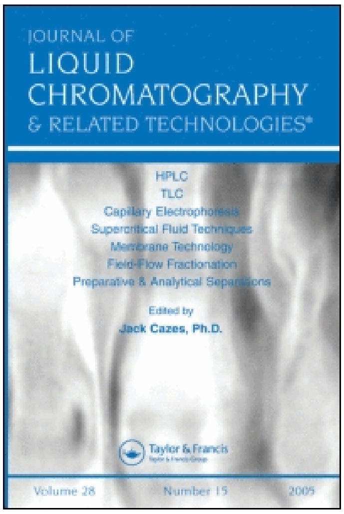

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THE KINETIC STUDY OF AGGREGATION OF THE SULPHIDE $Cu_{0.2}Zn_{0.8}S$ PARTICLES BY GRAVITATIONAL FIELD-FLOW FRACTIONATION

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ABSTRACT

Gravitational Field-Flow Fractionation (GFFF) is a sub-technique of FFF which combines the earth gravitational force with the carrier liquid flow in a horizontal, ribbon-like channel which is well suited for the separation and characterization of monodisperse or polydisperse colloidal materials and macromolecules.

In the present work the interaction between the polydisperse $Cu_{0.2}Zn_{0.8}S$ sulphide particles which leads to their aggregation is studied with the aid of the GFFF technique. From the variation of the number, average diameter of the particles with the time, rate constants for the bimolecular process of aggregation for the sulphide $Cu_{0.2}Zn_{0.8}S$, particles were determined and useful conclusions concerning the aggregation mechanism were extracted.

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INTRODUCTION

Gravitational field-flow fractionation (GFFF) is the experimentally simplest member of the family of field-flow fractionation (FFF) techniques.

FFF is a dynamic separation technique based on the differential elution of the sample constituents by a laminar flow in a flat ribbon-like, channel according to their sensitivity to an external field applied in the perpendicular direction to that of the flow.[1,2]

In GFFF an external force field of Earth's gravity causes the settlement of particles on the channel wall. There are also other forces acting on particles in the carrier the liquid flow-hydrodynamic lift forces.[3] These forces drive the particles away from the channel wall (in contrast to the gravitation) and focus them into narrow zones. The particles' size and the density of the particles determined the position of the zones in the flow velocity profile. So, in gravitational FFF, the interplay of steric interactions of the particles with the channel walls and the hydrodynamic lift force of various origins, lead to the larger particles moving more quickly than the smaller ones, and the separation mechanism is based more on the inherent particle size than on the ability of a particle to undergo Brownian diffusion.[4,5]

GFFF is a powerful, high resolution method which has been used successfully for separation and characterization of a wide variety and kind of colloids, micelles, blood cells, polystyrene latexes, glass beads, silicon particles, and biological macromolecules.[6-16]

The particle size distribution is the most important parameter for studying the colloid's stability and deposition on solid surfaces. In the present work, gravitational field-flow fractionation is used for the kinetic study of the aggregation of the $Cu_{0.2}Zn_{0.8}S$ sulphide particles.

EXPERIMENTAL

The GFFF system was built as described in detail, elsewhere.[17] The separation channel used in this work had the following dimensions: length L=100 cm, breadth a=1.0 cm, and thickness w=0.02 cm.

A Gilson Holochrome UV detector was used for detection at 254 nm and a Gilson Minipuls 2 peristaltic pump was used to pump the carrier solution and the sample to the channel.

The sample used in the present work was polydisperse irregular as has been shown by TEM pictures particles of the sulphide $Cu_{0.2}Zn_{0.8}S$, provided by Dr. E. Dalas, with number average diameter of (5.5 ± 1.8) μm.

The carrier solution was triply distilled water containing 0.5 % (v/v) of detergent FL-70 (Fisher Scientific Co.) and 0.02 % (w/w) of sodium azide (Fluka AG) as bacteriocide.

Twenty five microliters of the sulphide sample (concentration of 3 mg/cm^3) were injected into the GFFF channel. The relaxation time was 10 min, while the flow rate was 45 cm^3 h^{-1}. The same experiment was repeated at different times from the preparation of the sulphide sample, which was kept thermostated at 25°C while it was continuously agitated.

RESULTS AND DISCUSSION

In GFFF the diameter, $d_{i,}$, for spherical particles is given by the relation:

$$d_i = \frac{wV_0}{3\gamma}\frac{1}{V_r} = \frac{\lambda}{V_r} \qquad (1)$$

where w is the thickness of the channel, γ is the dimensionless factor which represents the complication of lift forces and related hydrodynamic effects,[16] V_r is the retention volume, and $\lambda = {}^{wV_0}\!/_{3\gamma}$.

For polydisperse samples the number average particle diameter is given by the equation:

$$d_N = \frac{\sum_i d_i N_i}{\sum_i N_i} = \frac{\lambda\left[\sum_i {}^{N_i}\!/_{V_{r_i}}\right]}{\sum_i N_i} \qquad (2)$$

while the standard deviation of the number average particle diameter by the relation:

$$\sigma_{d_N} = \left[\frac{\sum_i (d_i - d_N)^2 n_i}{\sum_i n_i - 1}\right]^{1/2} \qquad (3)$$

where N_i is the number of particles with constant diameter d_i. The parameter λ for the sulphide $Cu_{0.2}Zn_{0.8}S$ is 6.55 x 10^{-3} cm^4, as it was calculated from the Equation (2) using the value of d_N found from laser counter measurements with the values of V_{r_i} and N_i obtained from the fractogram.

The aggregation process described by the biomolecular kinetic equation:[18]

$$\frac{1}{N_i} = \frac{1}{N_0} + k_{app}t_i \tag{4}$$

where N_i is the total number of particles per unit volume at time t_i, N_0 is the initial number of the same particles and k_{app} is the apparent rate constant for the aggregation process.

The measurement of the independent kinetic units per unit volume, N_i, at different times t_i can give the rate constant for the aggregation. Considering that d_0 and d_i are the diameters of the spherical particles at initial time, t_0, and t_i, respectively, the corresponding volumes of the particles V_0 and V_i, are given by the relationships:

$$V_0 = \frac{1}{6}\pi d_0^3 \tag{5}$$

and $$V_i = \frac{1}{6}\pi d_i^3 \tag{6}$$

For polydisperse systems, as is the case in the present work, the d_0 and d_i can be replaced by the d_{N_0} and d_{N_i} respectively, and the Equation (4) gives:

$$d_{N_i}^3 = d_{N_0}^3 + d_{N_0}^3 N_0 k_{app} t_i \tag{7}$$

From the slope of the linear plot of the $d_{N_i}^3$ versus t_i the apparent rate constant, k_{app} can be determined. The N_0 value can be calculated from the ratio of the total volume of the injected sulphide solid sample, V_{tot}, to the volume of the particle, V_0, which can be determined by the Equation (5), using as d_0 the d_{N_0} value found from the intercept of the above plot. The V_{tot} can be found by the expression:

$$V_{tot} = {}^{V_i c_i}\!/_{\rho_i} \tag{8}$$

Figure 1(right). Fractogram of the sulphide $Cu_{0.2}Zn_{0.8}S$ particles obtained by GFFF after stirring of the sample at: (a) 5 hs, (b) 24 hs and (c) 95 hs. V_{r_1}, V_{r_2} and V_{r_3} are the respective retention volumes.

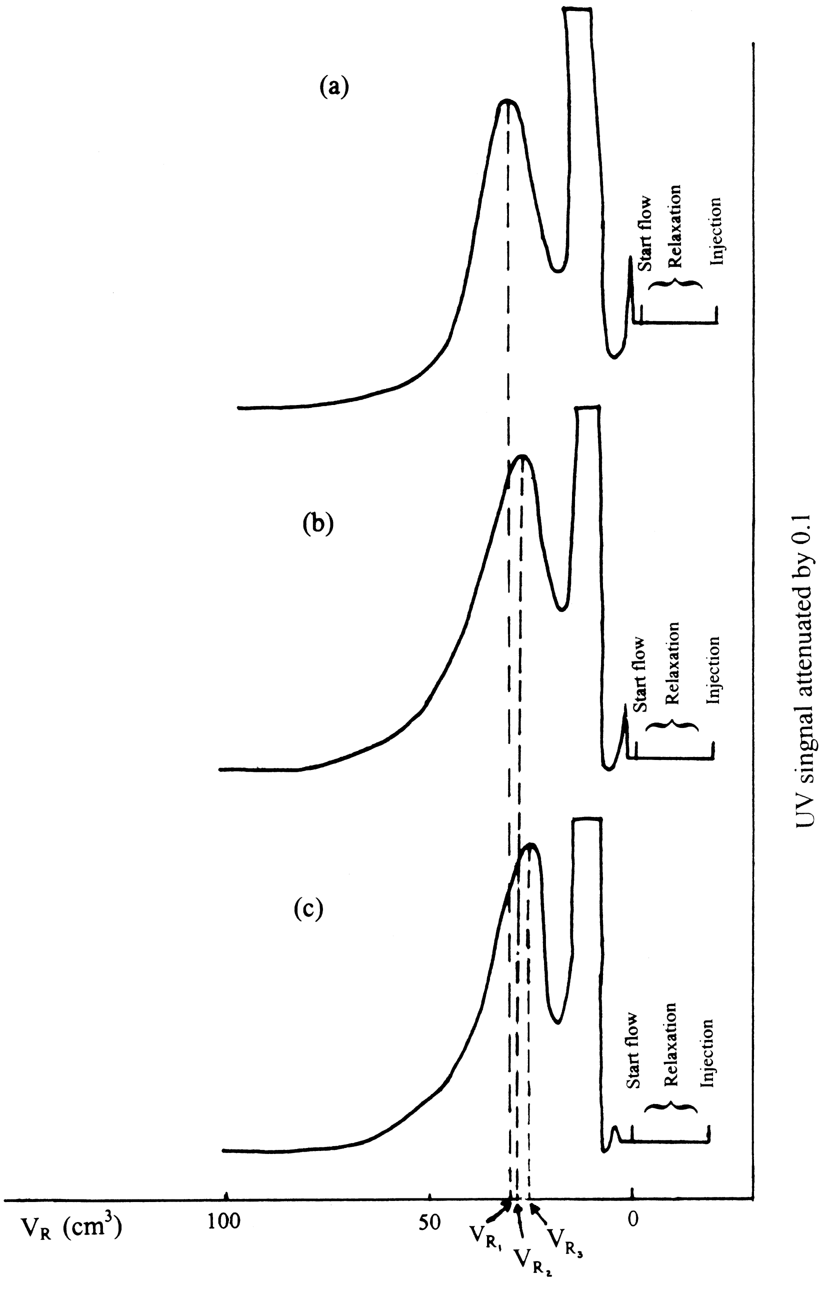
(a)
(b)
(c)
Start flow
Relaxation
Injection
Start flow
Relaxation
Injection
Start flow
Relaxation
Injection
V_R (cm³)
100
50
0
V_R1
V_R2
V_R3
UV singnal attenuated by 0.1

Table 1

Number Average Diameters d_N, of the Sulphide $Cu_{0.2}Zn_{0.8}S$ Particles with Their Standard Deviations σ_{d_N} at Different Times From the Preparation of the Sample Obtained by GFFF

Stirring Time (h)	$d_N \pm \sigma_{d_N}$ **(μm)**
3	5.339 ± 0.055
5	6.641 ± 0.069
9	6.518 ± 0.045
24	6.892 ± 0.070
31	6.901 ± 0.053
48	7.209 ± 0.037
68	8.060 ± 0.063
81	8.583 ± 0.011
95	7.864 ± 0.050
118	9.081 ± 0.051

where V_i is the injected volume, c_i is the concentration of the sample and ρ_i is the solid density. The solid density of the mixed sulphide ($Cu_{0.2}Zn_{0.8}S$) used was calculated by the densities of the pure ZnS and CuS sulphides to be 4.104 g cm^{-3}. Figure 1 shows the fractograms of the $Cu_{0.2}Zn_{0.8}S$ sulphide obtained by GFFF technique after 5, 24, and 45 hs. from the preparation of the sample.

The fractograms have the same morphology, but the respective retention volumes ($V_{r_j} V_{r_2}, V_{r_3}$) are changed with the time from the preparation of the sample. The calculated number average particle diameters with their standard deviations at different times from the sample's preparation are given in Table 1.

The plot of the d_N against the time from the preparation of the sample is shown in Figure 2. As one can see from that plot the value of d_n increases with increasing the time. After 118 hs from the preparation of the d_n sample the number average diameter becomes approximately double, due to the sample's aggregation process.

As mentioned earlier, the plot of d_N^3 versus t shown in Figure 3 is used to determine the apparent rate constant, k_{app}, for the aggregation process of the sulphide $Cu_{0.2}Zn_{0.8}S$ particles.

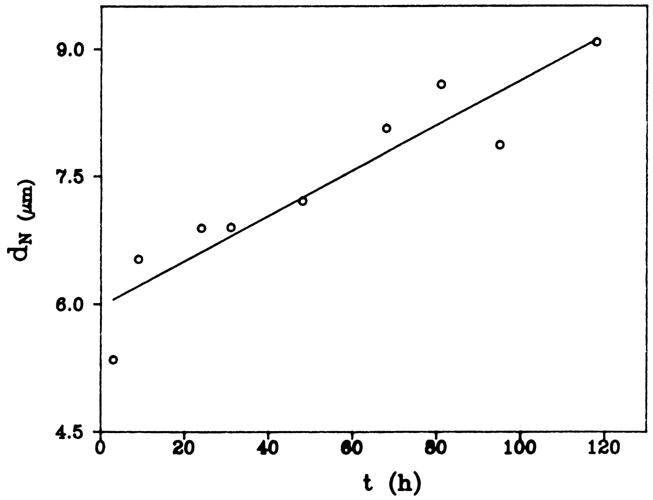

Figure 2. Variation of the number average diameter, d_N, for the $Cu_{0.2}Zn_{0.8}S$ particles with the time from the preparation of the sample.

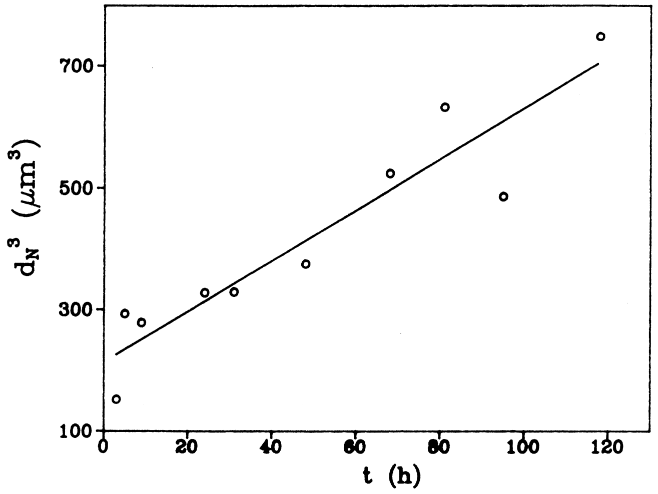

Figure 3. Plot of Equation (7) for the aggregation of $Cu_{0.2}Zn_{0.8}S$ particles dispersed in triply distilled water containing 0.5 % surfactant (v/v) FL-70 and 0.02 % (v/v) sodium azide.

In order to show whether the k_{app} value is determined solely by the rate at which two $Cu_{0.2}Zn_{0.8}S$ particles can diffuse to each other (diffusion control), or whether the rate of the aggregation process is limited by other slower process, we compare this value with the rate constant for the bimolecular collision (k_1) of the sulphide particles, as it can be calculated by Stoke-Einstein equation:

$$k_1 = \frac{8kT}{3n} cm^3 s^{-1} \qquad (9)$$

where n is the viscosity of the medium. The calculated value of $k_1 = 1.1 \times 10^{-11}$ cm^3 s^{-1} is about nine orders of magnitude greater than the experimental k_{app} value, showing that the aggregation rate is slower than that expected if the process was simply diffusion controlled. The latter indicates that the minimal mechanism for the aggregation process of the sulphide $Cu_{0.2}Zn_{0.8}S$ particles (SP) would be:

$$SP1 + SP2 \underset{k_{-1}}{\overset{k_1}{\Leftrightarrow}} \text{Intermediate complex} \xrightarrow{k_2} \text{Stable aggregation} \qquad (10)$$

where k_{-1} is the rate constant for the dissociation of the intermediate aggregate and k_2 is the rate constant for the process representing the rate-determining step in the aggregation reaction. Since k_{app}, describing the overall process of aggregation is smaller than the calculated k_1 value, there must be rapid equilibration of the individual sulphide particles and their intermediate complex followed by the slower step of irreversible aggregation.

As a general conclusion, the GFFF method can be used with success to study the aggregation process, and hence the stability of micron-sized polydisperse sulphide samples, which are of great importance in industrial and environmental chemistry.

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