SOLUBILITY OF PARTICULATE CADMIUM SULFIDE AT pH = 1–14: A RADIOTRACER STUDY

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Cadmium sulfide particles were prepared by precipitation from acid solution. A radio-tracer technique with ^{109}Cd was applied to measure the solubility of cadmium sulfide at various pH's. Filtration, centrifugation, ultracentrifugation, and dialysis were used to separate the particles from the solution. Only the last two techniques proved to be successful. The solubility of cadmium sulfide in water (pH = 7) is found to be: $7.9 \cdot 10^{-8} \text{ mol} \cdot \text{l}^{-1}$ in contrast with the literature value of $9.0 \cdot 10^{-6} \text{ mol} \cdot \text{l}^{-1}$. At low pH (1–4), the solubility agrees fairly well with the solubility calculated on the basis of generally accepted values for the solubility product and for the various complex formation constants, while at high pH (4–14) the solubility is higher than expected.

Introduction

In recent years there has been a growing interest in the characterization of aqueous cadmium sulfide suspensions. In various fields, e.g. photocatalytic splitting of water,^{1–3} waste water treatment technology,⁴ environmental research,⁵ soil chemistry,⁶ and biotechnology,⁷ quantitative information on the composition of the aqueous solution in equilibrium with cadmium sulfide is required.

In our laboratory material transport phenomena at the interface cadmium sulfide/aqueous solution in suspensions and the influence of visible light on these phenomena are studied. An important characteristic of these suspensions is the cadmium concentration in the solution in equilibrium with the solid phase: the solubility of the cadmium sulfide.

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The solubility of cadmium sulfide in water was determined experimentally as early as 1907^{8,9} and 1909.¹⁰ In spite of the criticism of KOLTHOFF¹¹ in 1931 on the validity of these results, the solubility of $1.3 \text{ mg} \cdot \text{l}^{-1}$ (Reference 9) is still given in compilations.^{12,13} Later, other determinations of the solubility product of cadmium sulfide were made¹⁴⁻¹⁶ and used to calculate the solubility at different pH values.^{17,18} However, experimental verification of the solubility calculated for various pH's has not been reported so far.

This study deals with the determination of the solubility of cadmium sulfide in the pH range 1–14. In addition, the experimental results will be compared with calculated values using various complex formation constants.

The radiotracer technique is suited for the determination of low solubilities. For this study ^{109}Cd appeared to be the most suitable radioisotope: it has a long half-life (453 d),¹⁹ it is measurable with high sensitivity and is commercially available. For a specific activity of $3 \cdot 10^{12} \text{ Bq} \cdot \text{mol}^{-1}$ a solubility down to $1.1 \cdot 10^{-12} \text{ mol} \cdot \text{l}^{-1}$ can be determined by liquid scintillation counting.

Experimental

Preparation of cadmium sulfide particles containing ^{109}CdS

The solubility experiments have been performed with the same type of cadmium sulfide suspensions as those being used for the studies of cadmium exchange at the solid/solution interface. These suspensions should contain discrete, well defined, particles preferably of the same size and with a diameter of 0.1 to 1.0 μm . Although this kind of particles may be prepared by homogeneous precipitation with thioacetamide,²⁰ this method was not followed, because its low yield (about 20%) is impractical when ^{109}Cd is to be incorporated into the particles. Instead, a hydrogen sulfide based precipitation procedure has been used throughout this work.

The solubility of cadmium sulfide was expected to be strongly dependent on pH: very low at high pH values and several orders of magnitude higher at low pH values. Consequently, ^{109}CdS -containing cadmium sulfide precipitates with a much higher specific activity would be needed for the solubility measurements at high pH than at low pH.

The tracer stock solution was prepared by diluting 1.0 ml of ^{109}Cd -cadmium chloride ($4.4 \mu\text{g} \cdot \text{ml}^{-1} \text{ Cd}$ and $29.6 \text{ MBq} \cdot \text{ml}^{-1} \text{ }^{109}\text{Cd}$ in 0.1M hydrochloric acid; Amersham, England; code: CUS. 1) to 10 ml with water. The radionuclide purity, as determined by Ge(Li) spectrometry, was at least 99.9%.

Analytical grade reagents and distilled water were used to prepare two solutions, containing (1) $2.5 \cdot 10^{-4} \text{ mol} \cdot \text{l}^{-1}$ cadmium chloride and (2) $4.0 \cdot 10^{-3} \text{ mol} \cdot \text{l}^{-1}$ cadmium chloride, both in 0.05M sulfuric acid. Prior to the precipitation, 80 μl of the tracer stock solution was added to 10 ml of the solution (1), resulting in batch 1 and 20 μl of the tracer stock solution to 50 ml of the solution (2), resulting in batch 2, respectively. After mixing thoroughly, a 0.1 ml sample was taken for the activity measurements. Hydrogen sulfide gas (99.95% pure) was led at a constant flow rate ($20 \text{ ml} \cdot \text{min}^{-1}$) through both batches, kept in 50 ml vessels, agitated by a magnetic stirrer and protected from light by black paper covering. After 10 minutes yellow-orange suspensions were obtained and the hydrogen sulfide flow was terminated. Samples of 10 μl were taken for examination by optical microscopy. The resulting precipitates were collected by filtration (cellulose nitrate membrane, pore size: 0.025 μm) and washed with distilled water.

The same procedure, but without adding the radioisotope, was followed to obtain similar precipitates to be used for their characterization. The dried precipitates were weighed in order to determine the yield, and studied by X-ray powder diffraction analysis. After redispersing in alcohol, deposition on a copper grid covered with a carbon film and drying in vacuum, the precipitates were studied by transmission electron microscopy combined with energy dispersive X-ray spectrometry (EDS).

Solubility experiments

Various amounts of sulfuric acid, hydrochloric acid, or sodium hydroxide, all of analytical reagent grade, were added to distilled water to obtain solutions of an appropriate pH. For the solubility experiments within the ranges pH 1–4 and pH 4–14 the ^{109}CdS containing cadmium sulfide precipitates from respectively batch 2 and batch 1, were dispersed directly from the filter membrane in 200 ml of the solution of appropriate pH by ultrasonic vibration. The suspensions contain, respectively, $1.25 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$ solid CdS from batch 1 and $1.0 \cdot 10^{-3} \text{ mol} \cdot \text{l}^{-1}$ solid CdS from batch 2. They were kept in closed 250 ml vessels (in order to avoid loss of hydrogen sulfide) and continuously agitated; A propeller stirrer instead of a magnetic stirrer was used to avoid crushing of the cadmium sulfide particles. The experiments were performed at 25 °C in the dark in order to prevent photochemical corrosion of the cadmium sulfide solid. At various time intervals a fraction of the suspension was collected.

Various separation techniques were applied to separate the particles from the solution before measuring the cadmium concentration in the solution: filtration, centrifugation and ultracentrifugation. A few characteristics of these techniques are sum-

Table 1
Properties of the separation techniques used

Technique	Membrane material	d, nm	ω , rad $\cdot$ s $^{-1}$	x_2/x_1	t, ks	r, nm
Centrifugation	—	—	398	3.2	3.6	32.2
Ultracentrifugation	—	—	3142	2.4	3.6	3.5
	—	—	3142	2.4	86.4	0.7
Filtration	Cellulose nitrate	25.0	—	—	—	12.5
Dialysis	Cellulose	2.4	—	—	—	1.2

where d — mean pore size,
 ω — angular velocity of the centrifuge rotor,
 x_2/x_1 — ratio of distances of the settling particles from the rotation center before and after centrifugation,
t — period of centrifugation,
r — radius of the separating particles, calculated using formula:²¹

$$r^2 = 9 \eta \log(x_2/x_1) / 2 \omega^2 t (\rho_p - \rho)$$

where η = viscosity of the solution (kg $\cdot$ m $^{-1}$ $\cdot$ s $^{-1}$), ρ_p and ρ are the densities (kg $\cdot$ m $^{-3}$) of the settling particles and the solution, respectively.

marized in Table 1. The radii of the particles separated by centrifugation and ultracentrifugation were calculated by means of the formula²¹ given in Table 1.

In some solubility experiments a dialysis technique was applied to separate the particles from the solution. The ^{109}CdS containing cadmium sulfide precipitate was dispersed from the filter membrane by ultrasonic vibration in 5 ml solution of an appropriate pH. A dialysis membrane bag (properties given in Table 1), containing this suspension, was transferred to closed 250 ml flasks, containing 200 ml of the same solution. This solution was agitated by a magnetic stirrer. The experiments were performed at 25 °C in the dark. At various time intervals 1.0 ml samples were taken from the dialysate.

When the cadmium concentration in the solution remained constant within 2% for at least seven days (corresponding with the relative standard deviation of the count rate), equilibrium was considered to have been reached, the final pH was measured, and the experiment was terminated. Equilibrium was usually reached after 14 days.

Liquid scintillation counting was used for detection of the radiation from ^{109}Cd . The samples were mixed with 10 ml of scintillation liquid Lumagel (Lumac/3m, Schaesberg, The Netherlands) and measured in a liquid scintillation counter for

1000 seconds. At $\text{pH} > 9$ it was necessary to add an amount (10 to 100 μl) of concentrated hydrochloric acid to the sample before mixing it with Lumagel, in order to suppress the quenching effect. The counting efficiency was $1.2 \text{ cps} \cdot \text{Bq}^{-1}$. The counting efficiency exceeds 1 because two transitions occur: ^{109}Cd decays to $^{109\text{m}}\text{Ag}$ by electron capture: 22 keV and 25 keV X-rays are emitted; $^{109\text{m}}\text{Ag}$ (39.8 s) decays to ^{109}Ag by isomeric transition, emitting 88.0 keV γ -rays and conversion electrons with energies of 62.5 keV and 84.2 keV.¹⁹

The cadmium concentration was calculated by comparing the radioactivity of the sample with that of the standard sample, taken from batch 1 and batch 2, and treated similarly as a real sample. From the specific activity of batch 1 ($9.5 \cdot 10^{10} \text{ Bq} \cdot \text{mol}^{-1}$) and batch 2 ($3.0 \cdot 10^8 \text{ Bq} \cdot \text{mol}^{-1}$), the counting efficiency ($1.2 \text{ cps} \cdot \text{Bq}^{-1}$), the counting time (1000 s) and the background value (1 cps), a detection limit has been derived. This limit is for batch 1: $8 \cdot 10^{-10} \text{ mol} \cdot \text{l}^{-1}$ and for batch 2: $3 \cdot 10^{-7} \text{ mol} \cdot \text{l}^{-1}$. A further decrease of the limit down to $10^{-12} \text{ mol} \cdot \text{l}^{-1}$ can be achieved by diluting ^{109}Cd with less stable cadmium.

Calculation of the solubility

The solubility of cadmium sulfide at a known (equilibrium) pH can be calculated from the (1) mass balance:

$$T_{\text{Cd}} = T_{\text{S}} \quad (1)$$

where T_{Cd} and T_{S} are the total amount of cadmium and sulfur in the solution, which is in equilibrium with solid cadmium sulfide and from the (2) solubility product:

$$K_{\text{sp}} = f_{\text{Cd}^{2+}} f_{\text{S}^{2-}} [\text{Cd}^{2+}] [\text{S}^{2-}] \quad (2)$$

where $f_{\text{Cd}^{2+}}$ and $f_{\text{S}^{2-}}$ are the activity coefficients of Cd^{2+} and S^{2-} .

The formation of the different complexes X_{ijklm} which contribute to the mass balance is represented in the following equilibrium equations:

with complex formation constants:

$$K_{ijklm} = \frac{fX_{ijklm} \left[X_{ijklm}^{2i-2j+k-l+mp} \right]}{f_{\text{Cd}^{2+}}^i f_{\text{S}^{2-}}^j f_{\text{H}^+}^k f_{\text{OH}^-}^l f_{\text{R}^p}^m [\text{Cd}^{2+}]^i [\text{S}^{2-}]^j [\text{H}^+]^k [\text{OH}^-]^l [\text{R}^p]^m} \quad (3)$$

Where the f 's are ionic activity coefficients, and R^p is a species representing SO_4^{2-} , Cl^- or CO_3^{2-} .

The total amount of cadmium is:

$$T_{\text{Cd}} = \sum_{i,j,k,l,m} i [X_{ijklm}^{2i-2j+k-1+mp}] \quad (4)$$

and the total amount of sulfur is:

$$T_{\text{S}} = \sum_{i,j,k,l,m} j [X_{ijklm}^{2i-2j+k-1+mp}] \quad (5)$$

The ionic activity coefficients have been calculated with the aid of the equation:²²

$$-\log f_z = 0.5 z^2 \left(\frac{I^{1/2}}{1 + I^{1/2}} - 0.3 I \right) \quad (6)$$

where f_z is the ionic activity coefficient of a z valent ion, and I is the ionic strength ($I = 1/2 \sum_i [i] z_i^2$) which is obtained by iteration from the final ion concentrations $[i]$. On combining Eqs (1)–(6) the concentration of the ionic species and the total amount of cadmium can be calculated.

Results and discussion

Characterization of cadmium sulfide particles

Optical microscopy (1000x) showed that the particles obtained were spherical submicron particles. The transmission electron micrograph (Fig. 1) shows that the particles, obtained from batch 1, have a rough surface. A similar appearance of particles from batch 2 is observed. The particle size distribution for 600 particles of the precipitate as shown in Fig. 2, is rather broad: The mean particle diameter and its standard deviation is $0.30 \mu\text{m}$ and $0.07 \mu\text{m}$ for batch 1, respectively, and $0.27 \mu\text{m}$ and $0.08 \mu\text{m}$ for batch 2, respectively. Comparison of the EDS analysis results of the precipitates from batch 1 and batch 2 with those of cadmium sulfide powder with known composition (Aldrich Chem. Comp. USA; code: 21, 792–1) shows that there is no excess of either cadmium or sulfur. The X-ray powder diffractograms showed the six major lines, characteristic of the hexagonal structure of cadmium sulfide crystals. These lines were weak and broad in comparison with

Fig. 1. Transmission electron micrograph of cadmium sulfide particles precipitated from batch 1

Fig. 2. The particle size distribution of cadmium sulfide particles precipitated from batch 1 and 2, as determined from transmission electron micrographs

cadmium sulfide particles with a mean diameter of $0.5\ \mu\text{m}$ (Aldrich Chem. Comp.). From approximate single size-strain analysis of the X-ray powder diffractograms, where it is assumed that the parameters measured are identical to those of a Voight function,^{2,3} the calculated mean effective crystallite diameter was 14 nm in the precipitate from batch 1, and 10 nm in the precipitate from batch 2. With regard to the particle size distributions in the precipitates from batch 1 and batch 2 it can be concluded that the particles are polycrystalline.

Measured solubility at different pH

Figure 3 shows the solubility of cadmium sulfide, expressed as the cadmium concentration in $\text{mol} \cdot \text{l}^{-1}$, as a function of pH obtained by separation via filtration or centrifugation. Above pH 5 the results scatter widely. Figure 4 gives results obtained using the dialysis and ultracentrifugation techniques. To the experimental data plotted as a function of the pH on a logarithmic scale two lines were fitted in, respectively,

Fig. 3. Logarithm of the cadmium concentration $[\text{Cd}]$ ($\text{mol} \cdot \text{l}^{-1}$) in samples as a function of the pH. Separation procedure: filtration ($\circ$) and centrifugation ($\bullet$); Linear regression lines (—) and corresponding 95% confidence areas (---)

the low (1–4) and the high (5–14) pH range. In order to allow an easy intercomparison of the data from Fig. 3 with those of Fig. 4, the 95% confidence areas are shown. These 95% confidence areas are constructed by using the 95% confidence limits for the intercept of the regression lines (assuming no uncertainty in the slope).

In the low pH range the data obtained by centrifugation and filtration (Fig. 3) agree with those obtained by ultracentrifugation and dialysis (Fig. 4). In the high pH range, however, only some incidental low values obtained by filtration and

Fig. 4. Logarithm of the cadmium concentration $[Cd]$ ($\text{mol} \cdot \text{l}^{-1}$) in samples as a function of the pH. Separation procedure: dialysis ($\circ$) and ultracentrifugation ($\bullet$). Linear regression lines and corresponding 95% confidence areas (shaded). The 95% confidence areas of the filtration and centrifugation (---) are transcribed from Fig. 3

centrifugation fall within the 95% confidence area of the ultracentrifugation and dialysis data. This, in addition to the smaller scatter of the ultracentrifugation and dialysis data, indicates that small particles (particle diameter between 7 nm and 25 nm, see Table 1) contributed to the measured cadmium concentration when filtration and centrifugation were used, but were largely removed by ultracentrifugation and dialysis.

Some experiments were performed to check the quality of the separation techniques used. When the ultracentrifugation duration was increased to 24 hours, the measured cadmium concentration did not change. Another check is to examine the effect of variations of the amount of cadmium sulfide precipitate added. When the amount of cadmium sulfide precipitate added was increased by at least a factor of 10, the cadmium concentration in the filtrate increased proportionally, but the cadmium concentration in the supernatant liquid, obtained by ultracentrifugation, remained unchanged. These experiments indicate a complete separation by the ultracentrifugation and dialysis techniques, so that experimental data, obtained by these techniques, give the real solubility of cadmium sulfide in aqueous solution.

If hydrochloric acid was used for pH adjustment instead of sulfuric acid, no change in solubility was observed. The influence of oxygen or carbon dioxide was checked by experiments carried out under argon with solutions from which oxygen and carbon dioxide were removed by a stream of argon. Again, no significant change was observed.

The experimentally determined solubility of cadmium sulfide in water (pH 7) amounts to $7.9 \cdot 10^{-8} \text{ mol} \cdot \text{l}^{-1}$; This value is significantly lower than the 80 years old value of $1.3 \text{ mg} \cdot \text{l}^{-1}$ ($= 9.0 \cdot 10^{-6} \text{ mol} \cdot \text{l}^{-1}$), which in spite of KOLTHOFF's criticism still appears in compilations of solubility data.

Figure 4 shows also that the solubility is strongly dependent on the pH at low pH values, while it is practically independent for values above 5. A similar slight pH dependence at higher pH, was reported by PETERS et al.²⁴ (black points in Fig. 5). He used ultrafiltration to separate cadmium sulfide particles from the suspension obtained by mixing solutions containing equimolar amounts of cadmium and sulfide.

Comparison between calculated and experimental solubility

In order to compare our experimental results with literature data, the solubility of cadmium sulfide at different pH values was calculated from the mass balance, the solubility product and the equilibrium constants for the complex formation reactions. Table 2 summarizes different sets of data for the solubility product and the forma-

Table 2
Values of the solubility product and complex formation constants (ionic strength $I = 0$)
used for the calculations of the solubility of cadmium sulfide

Curve	K_{S_0} $\text{mol}^2 \cdot \text{l}^{-2}$	K_{H_2S} $\text{mol}^{-1} \cdot \text{l}$	K_{HS^-} $\text{mol}^{-1} \cdot \text{l}$	K_{CdOH^+} $\text{mol}^{-1} \cdot \text{l}$	$K_{Cd(OH)_2}$ $\text{mol}^{-1} \cdot \text{l}$	K_{CdS} $\text{mol}^{-1} \cdot \text{l}$
b	$5.0 \cdot 10^{-28}$	$9.3 \cdot 10^6$	$1.0 \cdot 10^{15}$	$7.9 \cdot 10^3$	$6.3 \cdot 10^3$	—
Reference	16	25	25	26	26	
c*	$1.7 \cdot 10^{-26}$	$7.9 \cdot 10^6$	$3.0 \cdot 10^{13}$	$5.8 \cdot 10^{17}$	0	—
Reference	14	14	14	14	14	
d	$5.0 \cdot 10^{-28}$	$9.3 \cdot 10^6$	$1.0 \cdot 10^{15}$	$6.9 \cdot 10^{10}$	0	—
Reference	16	25	25		14	
e	$5.0 \cdot 10^{-28}$	$9.3 \cdot 10^6$	$1.0 \cdot 10^{15}$	$7.9 \cdot 10^3$	$6.3 \cdot 10^3$	$4.8 \cdot 10^{19}$
Reference	16	25	25	26	26

*Ionic strength $I = 1.0$

tion constants of HS^- , H_2S , CdOH^+ , $\text{Cd}(\text{OH})_2$, which were taken from literature (Data set b and c) or adjusted for giving better agreement with the experimental results (Data set d and e). Complex formation constants of other species^{25,26} were not varied, and ignored if their influence on the total cadmium concentration appeared to be negligible.

Fig. 5. Logarithm of the solubility ($\text{mol} \cdot \text{l}^{-1}$) as a function of the pH, calculated on the basis of the solubility product and complex formation constants, given in Table 2 (curve b, c, d, e). The linear regression lines (a) and corresponding 95% confidence areas (---), are transcribed from Fig. 4. Data, reported by PETERS et al.²⁴ (●).

In Fig. 5 the two lines, marked a, originate from Fig. 4, depicting the experimental solubility data. In the low pH range there is a satisfactory agreement between the experimental results and the calculations on the basis of generally accepted values (Data set b) of the various constants (Curve b in Fig. 5), but in the high pH range the experimental values are significantly higher and much less dependent on the pH than the calculated solubilities. Apparently, the Data set b does not sufficiently account for processes which become relevant at high pH values.

Curve c in Fig. 5 is calculated by using the equilibrium constants of STE-MARIE et al.¹⁴ (Data set c), corrected for the effect of ionic strength. Although there is no agreement between this curve and our experimental results, mainly because of a too high value for the complex formation constant of CdOH^+ , there is a resemblance in shape. The zero value for the complex formation constant of $\text{Cd}(\text{OH})_2$ is responsible for this shape, particularly with regard to the plateau at higher pH.

We have investigated the possibility of combining the merits of Curve b and c. As a result, Curve d is obtained from Curve b by replacing the value of the complex formation constant of $\text{Cd}(\text{OH})_2$ by zero and adjusting that of CdOH^+ so that the calculated curve at pH 13 becomes equal to the experimental value at this pH. Now, a rather good agreement between the calculated and experimental results is obtained.

However, another possible explanation for the plateau at higher pH could be the presence of undissociated cadmium sulfide in the solution, a phenomenon that has not been discussed in the literature so far. This consideration is represented by Curve e, where a fair agreement is obtained between experimental and calculated values by using Data set b under the assumption that the concentration of undissociated cadmium sulfide is equal to the experimental solubility at pH 13 (Data set e).

It should be noted that the experimental set-up does not allow (and was also not devised to do so) the verification of the assumption underlying the curves d and e.

The approach given above indicates that the large diversity of literature values for the solubility product and relevant complex formation constants may lead to considerable differences in calculated values and discrepancies from the experimental results. Therefore, experimental verification of calculated values remains indispensable.

Conclusions

The solubility of cadmium sulfide in water (pH = 7) has been determined to be $7.9 \cdot 10^{-8} \text{ mol} \cdot \text{l}^{-1}$.

Solubilities calculated on the basis of generally accepted values of the equilibrium constants agree with experimental ones only at low pH, while at higher pH values significant differences are found. The calculated curve may be fitted to the experimental one, by assuming the presence of undissociated cadmium sulfide or an enhanced concentration of CdOH^+ , while $\text{Cd}(\text{OH})_2$ is supposed to be absent in the solution.

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