SPECTROPHOTOMETRIC DETERMINATION OF SEDIMENTATION RATES OF CuS and BaS IN AQUEOUS MEDIA

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ABSTRACT
The sedimentation rates of CuS and BaS were determined by measuring the % transmittance with time of the metal sulphide precipitates in aqueous media. The results showed that the sedimentation rates of CuS decrease with increase in [Cu]$^{2+}$ at constant [S]$^{2-}$ and also with increase in [S]$^{2-}$ at constant [Cu]$^{2+}$. On the other hand, the sedimentation rates of BaS increase with increase in [Ba]$^{2+}$ at constant [S]$^{2-}$ and also with increase in [S]$^{2-}$ at constant [Ba]$^{2+}$ respectively, which showed a new trend of sedimentation rate. The overall sedimentation orders of CuS and BaS precipitates were first and second order sedimentations respectively implying that the processes were dependent on the precipitate concentrations.

1. INTRODUCTION
Wastewater treatment is a critical issue in the oil and Gas sector. The products of a number of reactions occurring in aqueous media are solids which may or may not deposit in the reaction medium upon formation. Depending upon the prevailing conditions or characteristics of the medium, the solids, often called precipitates (settle out of the solution) or remain suspended in the medium. A number of factors influence the settling out of solution of precipitates. Some of these factors include the molecular size of the precipitate, the density of the medium, the density of the precipitating particles, the viscosity of the medium, gravity, type or nature of precipitate (e.g crystalline or gelatinous) e.t.c, (Maron and Lando, 1974).

Precipitation reactions are important in unit operations of most industries (Earle, 1983). The formation of solid particles and their settling out of solution find ready application in water purification technologies, where coagulants and other precipitating agents are added to facilitate the settling out of solution of solids. Other applications of precipitation reactions include sewage effluent treatment, Imhoff tank (Van Nostrand, 1976), analytical separations (Skoog et al., 2004) and erythrocyte sedimentation rate, (ESR) studies (Westergren technique), (Cheesbrough, 2002), etc.

The settling out of solids from solutions under the force of gravity is often referred to as sedimentation (Hawley, 1981). Various types of precipitates settle out of aqueous solutions at different rates. The differences in the rates of sedimentation of substances are often exploited in analytical separations. Conditions can be adjusted in a medium to bring about the precipitation of a desired analyte, which may not favour the precipitation of other analytes that also have the potential to form precipitates.

Essien (1992,1994,1998; Mkpenie and Onwu, 2006) and Obunwo, et al. (2014) reported the
sedimentation rates of a number of insoluble salts by studying the variation of the height of precipitate formed and height of supernatant respectively as sedimentation progressed in a measuring cylinder. These studies formulated pseudo rate laws of sedimentation for the various salts and evaluated the orders of sedimentation of the constituent ions in a given salt.

The monitoring of sedimentation rates of various salts based upon measurements in the height of the precipitate or supernatant as a function of time could be subjective and the results may lead to determinate errors. Spectrophotometric method was recently adopted to monitor the sedimentation rates of PbS (Adiukwu, et al., 2008). Spectroscopy is a very reliable physical method used in kinetics studies (Davies, 1984). Transmittance,

\[
\text{Transmittance} = \frac{P}{P^0},
\]

which is the ratio of the power of the transmitted light against the incident light, is expected to vary as a function of time as the sedimentation process starts. Therefore the rate of variation of transmittance as a function of time is used in the evaluation of the sedimentation rates of precipitates.

However, this technique has not been used for the monitoring of the sedimentation rates of CuS and BaS respectively. \(\text{Ba}^{2+}\) and \(\text{Cu}^{2+}\) ions are commonly encountered ions in wastewaters from the oil and gas industry. For example, \(\text{Ba}^{2+}\) ions are applied, as densifiers in the drilling industry hence the knowledge of its sedimentation pattern in aqueous media may be necessary for unit designs.

1. MATERIALS AND METHODS

2.1 Materials

The salts used were all nitrate salts with sodium sulphide as the sulphide source. Barium nitrate was a product of Hopkin Williams Limited, England while copper nitrate trihydrate and sodium sulphide monohydrate were obtained from BDH chemicals Poole, England. These reagents were used without further purification. All transmittance measurements were carried out using Labo Med Inc. UV-VIS-2500.

2.2 Method

Stock solutions of 0.2M of the selected metallic nitrates and sodium sulphides were prepared. The working concentrations of the metal ions and sulphide ions, 0.001M to 0.1M were obtained through dilution. Varying concentrations of the metal ions (0.001M to 0.005M) and a constant concentration (0.1M) of the sulphide ion were mixed to form the metal sulphide precipitates and vice versa when the metal ion concentrations were kept constant. The various precipitates of the metal sulphides upon formation were immediately transferred to a cuvette and the transmittance was measured, using a digital stopwatch and deionized water as the blank.
2.3 Sedimentation rate/Sedimentation order determination:
Graphical plot of the changes in transmittance as a function of time gave the sedimentation rate curve of the metal sulphide precipitate. The sedimentation rate was evaluated from the slope of the tangent to this curve by the method of initial rates (Whitten et al, 2000). The slope of the plot of the negative logarithm of the initial sedimentation rates versus the negative logarithm of the concentrations of the ion was obtained as the sedimentation order and the intercept, the sedimentation rate constant. Sedimentation rate, \( (R_s) \) may be expressed as Equation 1 (Maron and Prutin, 1965).

\[
R_s = \frac{2r^2g(\rho - \rho')}{{9\eta}}
\]  

(1)

where \( r \) = radius of the settling particle, \( g \) = acceleration due to gravity, \( \eta \) = viscosity of liquid medium, \( \rho \) = density of the settling particle, \( \rho' \) = density of the liquid medium.

The sedimentation rate, \( R_s \) was measured in terms of the variation in percentage transmittance (d%\( T \)) with time (dt). The %\( T \) was deduced from the optical density or absorbance of the sedimenting particles. That is;

\[
%T = 10^{(2-A)}
\]

(2)

where \( A \) = absorbance, %\( T \) = percentage transmittance, Equation (1) can therefore be written as

\[
\frac{\partial%T}{\partial t} = \frac{2r^2g(\rho - \rho')}{9\eta}
\]

(3)

The mass of the setting particle at any given time depends upon the concentration of the particle. Hence sedimentation rate, \( R_s \) can be expressed as a pseudo rate order law (Equations 4 and 5) according to Essien (1992).

\[
R_s \propto [M^{2+}]^a [X^{2-}]^b \quad \text{Or} \quad R_s = k [M^{2+}]^a [X^{2-}]^b = \frac{\partial%T}{\partial t}
\]

(4)

\[
\log R_s = \log k + a \log [M^{2+}] + b \log [X^{2-}]
\]

(5)

For divalent metal sulphides; \( R_s \) = Sedimentation rate, \([M^{2+}]\) = divalent metal ion concentration, \([X^{2-}]\) = divalent anion (sulphide) concentration, \( k \) = sedimentation rate constant, (for cation or anion depending on the ion that was varied) \( a \) = cation sedimentation order, \( b \) = anion sedimentation order.

3. RESULTS AND DISCUSSION
The results of the sedimentation rates and \(-\log\) rates evaluated from Equations 4 and 5 for varying \( Cu^{2+} \) and \( Ba^{2+} \) ions at constant sulphide ion concentration are shown in Table 1. The sedimentation rate of CuS precipitates decrease with increase in the concentration of Cu\(^{2+}\) ions.
The highest value recorded at 0.001M was 0.2056 %T/sec while the least, 0.0995 %T/sec was at 0.005M (See the downward trend from left to right on the plot in Figure 1a). Similar trend has been reported in literature (Essien, 1992, 1994, 1998; Mkpenie and Onwu, 2006).

Conversely, the sedimentation rate of BaS precipitates increase with increase in the concentration of Ba$^{2+}$ ions. These are shown in Tables 1 and Figure 1b. The sedimentation rate trend was similar to that of PbS precipitate reported by Adiukwu, et al (2008). The reason for this new trend has not been fully understood and is recommended for further studies. The magnitude of the sedimentation rates of Ba$^{2+}$ were however lower than those of the Cu$^{2+}$ ions. The highest sedimentation rate of Ba$^{2+}$ ions recorded was 0.0575 %T/sec at 0.005M.

Table 1. Sedimentation Rates Rs, (%T/sec) of various concentrations of metal sulphides formed from mixing 0.100M sulphide ion and varying concentrations of the Metal ions

<table>
<thead>
<tr>
<th>Samples</th>
<th>Conc (Moldm$^{-3}$) of Metal ions</th>
<th>0.0010</th>
<th>0.0020</th>
<th>0.0030</th>
<th>0.0040</th>
<th>0.0050</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>- Log Conc.</td>
<td>3.0000</td>
<td>2.7000</td>
<td>2.5200</td>
<td>2.4000</td>
<td>2.3000</td>
</tr>
<tr>
<td>CuS</td>
<td>Sedimentation Rate, Rs (%T/sec.)</td>
<td>0.2056</td>
<td>0.1300</td>
<td>0.1176</td>
<td>0.1000</td>
<td>0.0995</td>
</tr>
<tr>
<td></td>
<td>-log Rs</td>
<td>0.6870</td>
<td>0.8861</td>
<td>0.9296</td>
<td>1.0000</td>
<td>1.0022</td>
</tr>
<tr>
<td>BaS</td>
<td>Sedimentation, Rate Rs (%T/sec)</td>
<td>0.0208</td>
<td>0.0125</td>
<td>0.0325</td>
<td>0.0250</td>
<td>0.0575</td>
</tr>
<tr>
<td></td>
<td>- log Rs</td>
<td>1.6819</td>
<td>1.9030</td>
<td>1.4880</td>
<td>1.6020</td>
<td>1.2403</td>
</tr>
</tbody>
</table>

The sedimentation rate constant and sedimentation order with respect to Cu$^{2+}$ ions were $5.01 \times 10^{-3}$ (mol/dm$^3$)$^{1-n}$ and $-0.55$ respectively (Table 2) while the sedimentation rate constant and sedimentation order of Ba$^{2+}$ ions were $3.98 \times 10^2$(mol/dm$^3$)$^{1-n}$ and 1.63, respectively. The sedimentation orders, (a) and sedimentation rate constants of the two metal sulphides at constant sulphide ion concentration, [S$^{2-}$] were of the trend BaS>CuS. The lower molar mass and density may account for this trend.
Sedimentation rate constants and sedimentation orders of the metal sulphide precipitates formed from the mixing 0.100M sulphide ions and varying concentrations of the metal ions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Derived K from the graph $k_m$, $(moldm^{-3})^{n(s)}$</th>
<th>a</th>
<th>(a+b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuS</td>
<td>$5.01 \times 10^{-3}$</td>
<td>-0.55</td>
<td>-1.05</td>
</tr>
<tr>
<td>BaS</td>
<td>$3.98 \times 10^2$</td>
<td>1.63</td>
<td>1.95</td>
</tr>
</tbody>
</table>

The sedimentation rates of CuS precipitates decreased with increase in the concentration of the sulphide ions. See Table 3 for the data and Figure 1c for the pattern. The concentration of large ions of the media (excess reagent) may also be responsible for this trend. This could decrease the sedimentation rate as well as the sedimentation order. The highest sedimentation rate recorded for CuS precipitates was 0.1825%T/sec at 0.100M. The sedimentation rate constant and the sedimentation order (b) were $7.08 \times 10^{-3}$ (moldm$^{-3}$)$^{1-n(s)}$ and -0.50 respectively.

BaS precipitates also had increase in sedimentation rates with increase in the concentration of the sulphide ions, $S^{2-}$. The sedimentation rates shown in Table 3 and Figure 1d respectively had similar trend with those obtained at constant sulphide ion concentration, [$S^{2-}$]. The values of the sedimentation rates and sedimentation rate constants were also lower than the values obtained at constant sulphide concentration [$S^{2-}$].

<table>
<thead>
<tr>
<th>Samples</th>
<th>Conc (Moldm$^{-3}$) of Metal ions</th>
<th>0.0010</th>
<th>0.0020</th>
<th>0.0030</th>
<th>0.0040</th>
<th>0.0050</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>- Log Conc.</td>
<td>3.0000</td>
<td>2.7000</td>
<td>2.5200</td>
<td>2.4000</td>
<td>2.3000</td>
</tr>
<tr>
<td>CuS</td>
<td>Sedimentation Rate, Rs (%T/sec.)</td>
<td>0.1825</td>
<td>0.1575</td>
<td>0.1250</td>
<td>0.1125</td>
<td>0.0775</td>
</tr>
<tr>
<td></td>
<td>- log Rs</td>
<td>0.7387</td>
<td>0.8027</td>
<td>0.9031</td>
<td>0.9488</td>
<td>0.1111</td>
</tr>
</tbody>
</table>
The sedimentation rate constant and order obtained at constant [Ba\(^{2+}\)] was 1.78x10\(^{-1}\) (moldm\(^{-3}\))\(^{-1}\)\(n(s)^{-1}\) and 0.32 respectively which is approximately zero order sedimentation as shown in Table 4. The following equations can be written for the sedimentation process of the metal sulphides studied based upon the results obtained;

CuS: \[ \text{Rs} = K [\text{Cu}^{2+}]^{0.55} [\text{S}^{2-}]^{0.5} \]  
BaS: \[ \text{Rs} = K [\text{Ba}^{2+}]^{1.63} [\text{S}^{2-}]^{0.32} \]

The negative signs in equations (7 and 8) showed that such sedimentation rate decreased with increase in the concentration of the precipitating ions.

Table 4. Sedimentation rate constants and sedimentation orders of the metal sulphide precipitates formed from the mixing 0.100M metals ions and varying concentrations of the sulphide ions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Derived K from the graph (k_m), (moldm(^{-3}))(^{-1})(n(s)^{-1})</th>
<th>a</th>
<th>(a+b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuS</td>
<td>7.08 X 10(^{-3})</td>
<td>-0.50</td>
<td>-1.05</td>
</tr>
<tr>
<td>BaS</td>
<td>1.78 X 10(^{-1})</td>
<td>0.32</td>
<td>1.95</td>
</tr>
</tbody>
</table>

The sedimentation order and the sedimentation rate constants agreed with their molecular masses and sizes. Presented below are Figures (1c and d) showing the patterns of sedimentation at constant sulphide ion concentration, [S\(^{2-}\)].
The sedimentation orders of the two metal sulphides at constant metal ion concentrations, $[M^{2+}]$ were of the trend, CuS>BaS. The trend agreed with their molecular densities. A sedimentation rate is largely dependent on molecular densities, equation 1 by Maron and Putin (1965). The sedimentation rate constant trend was BaS>CuS, a reverse of their molecular densities. The overall sedimentation order of BaS precipitates was second order sedimentation, and CuS, first order overall sedimentation. The overall sedimentation order trend was BaS>CuS.

4. CONCLUSION
The spectrophotometric determination of sedimentation rates of CuS and BaS has been reported. The results showed that the sedimentation rate of CuS decreased with increase in $[Cu^{2+}]$ at constant $[S^{2-}]$ and also with increase in $[S^{2-}]$ at constant $[Cu^{2+}]$ while that of BaS increased with increase in $[Ba^{2+}]$ at constant $[S^{2-}]$ and also with increase in $[S^{2-}]$ at constant $[Ba^{2+}]$ respectively, with the latter being a new, unconventional trend. This report provides analytical data that can be used in sedimentation rate studies and design of sedimentation tanks for oil and gas industries.
Gas wastewater. The results showed that the technique is effective and reliable. The choice of a common medium by using nitrates of all the salts provided a medium of identical ionic strength for the studies. Particle shape or crystal structure, and ion-ion/ion solvent interaction are some of the factors not expressed by Stoke's law of sedimentation but may contribute immensely to the dynamics of sedimentation and is recommended for further studies.

5. REFERENCES


