Determination of Sedimentation Rates of Cobalt II Insoluble Compounds and Absorption Coefficients of the Sedimenting Particles using Gamma Radiation

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Summary: Studies on the sedimentation rates of cobalt II insoluble compounds show that the chromate and sulphide have higher sedimentation rates of 4.38 cm^3 min^{-1} and 5.90 cm^3 min^{-1} respectively while the cyanide had the lowest sedimentation rate of 0.230 cm^3 min^{-1}. The cyanide, chromate and sulphide show first order sedimntations while the carbonate and hydroxide show half order sedimentations. The sedimentation constant increases with increase in sedimentation rate.

The carbonate had the lowest mass absorption coefficient of 0.014 cm^2g^{-1} while the chromate had the highest mass absorption coefficient of 0.071 cm^2 g^{-1} and absorption coefficient has a linear dependence on the sedimentation rate.

Introduction

There are many chemical reactions that form solid deposits which are called precipitates. The precipitated solids are often called insoluble compounds. When the precipitates are formed in a liquid medium, the rate of free settling of the precipitates can be termed as sedimentation rate. According to Hawley [1], sedimentation is defined as the free settling out of small particles in liquid or gaseous suspension by gravity or that resulting from a chemical reaction. Studies on sedimentation resulting from chemical reaction can lead to the determination of sedimentation rates, sedimentation constant and sedimentation orders of insoluble compounds. The above parameters have earlier been determined for the insoluble transition metal hydroxides [2] copper II and zinc insoluble compounds [3,4]. The effect of temperature on sedimentation rate has been studied in copper II insoluble compounds and the results show Arrhenius-type behaviour as in the rate of chemical reactions [3].

Gamma rays have been used to study particles absorption coefficients of insoluble materials [5], absorption coefficients of clays and laterites used as building materials [6], densities of rocks and other materials [7,8].

We assume here that the absorption coefficient is a factor related to the particle size of the insoluble sedimenting compounds. In this study, the sedimentation rates and other sedimentation parameters for cobalt II insoluble compounds are reported and the absorption coefficients for the insoluble compounds are determined using gamma irradiation from ^{60}Co source. The results are used to explain the differences in the free sedimentation rates of the cobalt II insoluble compounds.

Results and Discussion

The rate of sedimentation (Rs) has earlier been expressed mathematically with respect to the concentrations of the ions forming the precipitates [2] as:

$$Rs = k\,(M)^a(A)^b \qquad (1)$$

where

k is the sedimentation constant

(M) is the concentration of the metal ion

(A) is the concentration of the anion,

(the precipitating agent).

a and b are the orders of the sedimentation.

The concentrations of cobalt II ions in all our reactions were kept constant at 0.1M., and the sedimentation constant k was the constant for the free settling of the formed precipitates. With these conditions are we can deduce equation (1) above to read:

$$Rs = k'(A)^b \qquad (2)$$

where $k' = k\,(M)^a$

By plotting ln Rs versus ln (A), the slope of the straight line gives the result for b, the sedimentation order while the intercept gives the result for the sedimentation constant for the precipitating compounds.

The results for the above plots are presented in figure I for the insoluble compounds of cobalt II. The sedimentation orders and constants are presented on Table-1 for the individual insoluble cobalt II compounds. The cyanide, chromate and sulphide of cobalt II had sedimentation orders of 0.830, 0.860 and 0.880 respectively, which were all grouped as first order while the carbonate and hydroxide had 0. 530 and 0.500 respectively which were half order sedimentations. The sedimentation constant ranges between 5.96×10^{-2} min^{-1} to 12.2×10^{-1} min^{-1} for the cyanide and sulphide respectively.

The results presented on figure 1 were obtained by studying the reactions forming the precipitate at varying concentrations of the precipitating agents. The sedimentation rates of the stoichiometric reaction of cobalt ions with the precipitating agents are presented on Table-1. It was observed that the sedimentation rate decreases with increase concentrations of the precipitating agents as observed earlier [2-4]. Cobalt II sulphide had the highest sedimentation rate of 5.90 cm^3 min^{-1} while the cyanide had the lowest sedimentation rate of 0.23 cm^3 min^{-1}. As shown on Table-1, there was a gradual increase in the sedimentation rate as the sedimentation constant increases from $Co(CN)_2$ to CoS., and also as the density increases. Fig. 2, shows the variation in absorption of gamma radiations with thickness, d of the sedimenting particles. The transmitted intensity of the gamma radiations, I through the sample is given by

$$I = I_o\, e^{-\&d} \qquad (3)$$

where I_o is the incident intensity and

& is the absorption coefficient

Thus, the absorption coefficient is obtained as the slope of a plot of ln (I_o/I) against d. The respective absorption coefficient for the insoluble cobalt II compounds are presented in Table-1. Results show that the absorption coefficient increases with increase in sedimentation rate. The fast moving CoS and $CoCrO_4$, absorb or scatter more of the radiations than the slow moving $Co(CN)_2$, $CoCO_3$ and $Co(OH)_2$. From figure 3, it is observed that the absorption coefficient has a linear dependence on sedimentation rate of insoluble cobalt II compounds, mostly with the low sedimenting particles. The deviation observed with the fast sedimenting particles is attributed to multiple absorption and scattering of the gamma radiation due to high density, high momentum as well as the large size of the particles [6,7].

The particles here refer not only to the individual mechanical separates but also to the

Table-1: Results for sedimentation of insoluble compounds of cobalt II

Insdoluble compound	Sedimentation Rate $cm^3 min^{-1}$	Sedimentation Order	Sedimentation constant (min^{-1})	Paticle Absorption Coefficient (cm^{-1})	Determined Density of the compound $g cm^{-3}$	Mass Absorption Coefficient of the compounds ($cm^2 g^{-1}$)
$Co(CN)_2$	0.230	0.830	5.96×10^{-2}	0.043	1.800	0.024
$CoCO_3$	0.461	0.530	1.35×10^{-1}	0.051	3.680	0.014
$Co(OH)_2$	0.750	0.500	3.50×10^{-1}	0.054	3.450	0.016
$CrCrO_4$	4.380	0.860	6.48×10^{-1}	0.213	3.000	0.071
CoS	5.900	0.880	12.21×10^{-1}	0.271	3.850	0.070

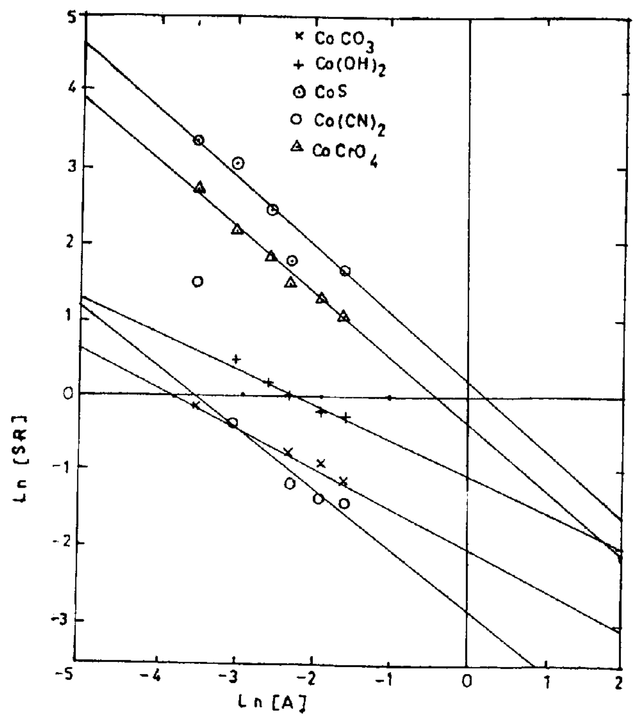

Fig. 1: Variation in sedimentation rate (SR) with concentration of precipitating agent (A).

aggregates or structural elements which have been formed by the aggregation of smaller mechanical functions [9].

Since sedimentation rate depends on several factors some of which include density and size of the particles, absorption depends also on those factors. High density particles absorb or scatter more radiations than the low density particles [6,10]. Large particles have greater pore spaces than the small sized particles [9], and therefore absorb or scatter less radiations than the small sized particles, since those radiations passing through the pore spaces encounter little resistance. The mass absorption coefficients were calculated by dividing the absorption coefficient by the density of the insoluble compound. The results are presented on Table-1 and $CoCrO_4$ had the greatest mass absorption coefficient of 0.071 cm^2/g while $CoCO_3$ had the least mass absorption coefficient of 0.014 cm^2/g. The particles of CoS and $CoCrO_4$ have faster sedimentation rates and are probably larger than those of $CoCo_3$, $Co(CN)_2$ and $Co(OH)_2$.

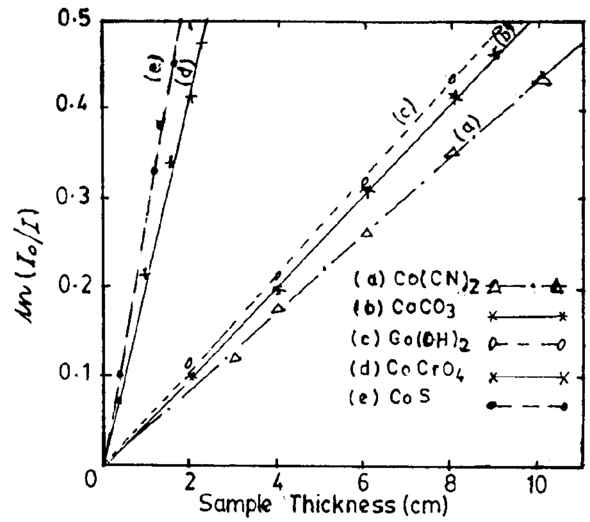

Fig. 2: Variation in absorption of gamma radiation with thickness of sedimenting cobalt II compounds.

Therefore larger particles of CoS and $CoCrO_4$ have higher values of absorption coefficients and mass absorption coefficients as observed on Table-1; eventhough there is no clear relationship between the mass absorption coefficients and the sedimentation rates for the cobalt II insoluble compounds. The overall results seem to suggest that CoS and $CoCrO_4$ particles have structures and bonding types that are quite different from those of $CoCO_3$, $Co(OH)_2$ and $Co(CN)_2$ particles. In conclusion we can use gamma ray absorption technique to study the sedimentation rates and absorption of gamma radiations of sedimenting particles of insoluble inorganic compounds.

Experimental

(a) Determination of sedimentation rates

The experimental procedure for the determination of sedimentation rates was similar to the one described earlier [2,3]. Cobalt nitrate was used for the preparation of the Co^{2+} ions and 0.1M solution was used for all the reactions. Solutions of the precipitating agents were prepared from sodium hydroxide pellets, sodium trioxocarbonate IV, sodium sulphide, sodium cyanide and potassium tetraoxochromate VI salts with concentrations ranging from 0.03M to 0.20M. Twenty ml of the cobalt ions were gently added to 20 ml of the precipitating agents in 100-ml measuring cylinder, stirred and allowed to stand. Volumes of the precipitate were recorded at given time intervals. The plots of change in volume versus time were made for each run and the results presented are the average of the three runs.

(b) Determination of absorption coefficient

The experimental set up for this determination was as described earlier in our previous studies [4]. The set up comprised of a GM tube connected to a scalar/timer. The sample

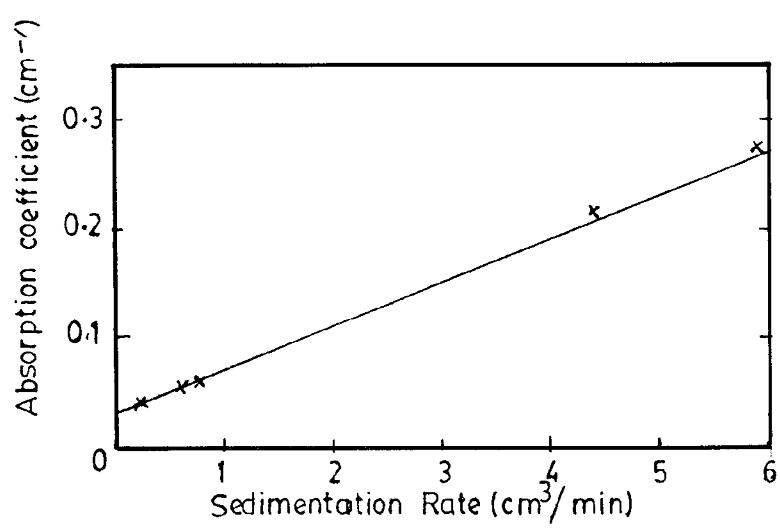

Fig. 3: Dependence of absorption coefficient on sedimentation rate of cobalt II compounds.

container was a graduated measuring cylinder which contained the precipitated insoluble cobalt compound. The liquid medium was removed by decantation and the height of the precipitate was measured as the sample thickness. The measuring cylinder was placed over the ^{60}Co used as the gamma-ray irradiation source. The source, the sample container and the detector were arranged vertically and axially. The count with the empty measuring cylinder was taken and the total count recorded as I_o. The total number of counts when the insoluble compound was added was recorded as I. The counting were done for one hour period. The precipitates were finally filtered, oven-dried, weighed and their densities were measured by weighing and displacement method.

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