Determination of Effects of Some Parameters On The Sedimentation Rates Of Strontium And Barium Carbonates In Aqueous Medium.

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Abstract: *In recent times sedimentation data have become increasingly relevant in modeling sedimentation operations such as filtration, fluidization, two-phase flow operations and in environmental engineering. In this study, the effects of reactants concentrations and size of settling vesselson the sedimentation rates of strontium and barium carbonates, in aqueous medium, were studied by a modified approach of the 'isolation method'. We systematically varied the interactions and chemical environment of the resulting precipitates by successively varying the concentrations of ions in excess in the mixtures. This variation affected the kinetic behaviour of the precipitates in the suspension medium and the results obtained showed a relationship between the sedimentation behaviour of the insoluble metal carbonates and the ionic concentrations of the reactants. Initial settling behaviour also showed that, for the colloidal precipitates, increasing excess of metal ions in reaction mixture had more significant effect than increasing excess carbonate ions. When the metal ion concentration was varied, +0.21 and -0.67 were obtained as sedimentation order and 1.01×10^{-1} cm $s^{-1}M^{-1}$ and 2.32×10^{-3} cm $s^{-1}M^{-1}$ were also obtained as sedimentation rate constants for strontium and barium carbonates respectively. On the other hand, when the carbonate ion concentration was varied, +0.35 and -1.01 were obtained as sedimentation orders and 1.36×10^{-1} cm $s^{-1}M^{-1}$ and 3.81×10^{-4} cm $s^{-1}M^{-1}$ were also obtained as sedimentation rate constants for strontium and barium carbonates respectively. The results of the sedimentation rates of barium carbonate precipitates measured in cylinders of varying sizes showed that the rate correlated positively ($r^2 = 0.9056$) with the internal diameter of the cylinders.*

Keywords: *Sedimentation, Sedimentation rate, Sedimentation order, Sedimentation rate constant, $SrCO_3$, $BaCO_3$*

I. Introduction

The principle of sedimentation, which involves the settling of heavy particles towards the foot of a column of solution in a gravitational field, has been applied in a number of chemical engineering operations such as filtration, fluidization, two-phase flow operations and environmental engineering. Sedimentation rate data have been employed in metallurgical practices for separating suspended solid particles from liquid (Senthilkumar, *et. al.*, 2008).

In sedimentation studies, various factors, such as particle size distribution, shape, density, pressure gradients and flocculation (Nilufer, 2006; Nongkran&Apinon,2008) have been identified to affect settling characteristics of particulate suspension.

Sedimentation process is, however, distinct from precipitation, in which a separable solid phase is produced within a liquid medium. These solid particles may then settle, if left to stand, at the bottom under gravity, as sediments. The free settling of the precipitates under gravity can be monitored to determine sedimentation rates, sedimentation constants and sedimentation orders of the insoluble compounds (Essien, 1992, 1998; Essien and Ekpe, 1998 and Mkpenie and Onwu, 2006).

In this study, the effects of reactants concentrations and size of settling vessels on the sedimentation rates of strontium and barium carbonates, in aqueous medium, were carried out by a modified approach of the 'isolation method'.

II. Materials And Methods

All salts including, $Sr(NO_3)_2$, $Ba(NO_3)_2$, and Na_2CO_3 (anhydrous) were weighed on a scout pro digital balance and their solutions prepared with triply distilled water. Various sizes of measuring cylinders and volumetric flasks as well as other pieces of glassware were thoroughly washed clean with the distilled water.

Sedimentation Rate measurement

The experimental procedure employed is similar to that described in our previous study (Obunwo *et al.*, 2014). It involved the modified approach ofthe method of initial rates (Raymond, 1981; Atkins & Paula, 2006)

of sedimentation of precipitates formed, at the beginning of settling process. All experiments were carried out at the ambient morning hour temperatures ranging between 27.5 – 29.0^{o}C.

Standard solutions of strontium nitrate and sodium carbonate (precipitating agent) were prepared in concentrations ranging between 0.01M and 0.11M. By mixing equal volumes of the solutions containing the cations and the anions in a 100ml measuring cylinder, precipitates were formed. The cylinder was bench-mounted and provided with back lighting (100-watts white fluorescent bulb) to enhance illumination and accurate monitoring (Armfield, 2011 and Obunwo *et al.*, 2014). Sedimentation of the precipitates was monitored by varying the initial concentrations of the cations (Sr^{2+} or Ba^{2+}) while keeping the carbonate ions (precipitating agent) concentrations constant. This procedure is then reversed by varying the concentrations of the carbonate ions and keeping the concentrations of the cations constant.

The change in height (CH) of the precipitate was plotted against the settling time (t) and the sedimentation rate (Rs) was calculated from the slope. Other sedimentation parameters were further derived from those plots.

III.   Results And Discussion

The sedimentation rate, Rs, is expressed mathematically (Essien, 1992) as

$R_s = \dfrac{dx}{dt} = Ks[A^{+n}]^a[B^{-m}]^b.$ (1)

The empirical sedimentation orders, (a) and (b), and constant, Ks, were evaluated using equation (1), as

$Log\ Rs = Log\ Ks + a\ Log\ [M^{2+}] + b\ Log\ [CO_3^{2-}]$ (2)

When $[M^{2+}]$ is isolated (or kept constant),

$Log\ Rs = Log\ ks_1 + b\ Log\ [CO_3^{2-}].$ (3)

Again, when $[CO_3^{2-}]$ is isolated (or kept constant)

$Log\ Rs = Log\ ks_2 + a\ Log\ [M^{2+}].$ (4)

ks_1 and ks_2 are the sedimentation rate constants with respect to the cations and anions respectively.

In this study, carbonate precipitates were formed by the chemical reaction illustrated in equation 5.

$M(NO_3)_{2(aq)} + Na_2CO_{3(aq)} \rightarrow MCO_{3(s)} + 2NaNO_{3(aq)}$ (5)
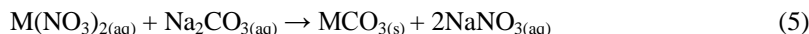
The italicized M in equation 5 represents Strontium or Barium in the precipitation process.

Table 1: Sedimentation Rate parameters of strontium carbonate and barium carbonate precipitates

precipitate	Sedimentation order (a) at constant $[CO_3^{2-}]$	Sedimentation constant (ks_1) at constant $[CO_3^{2-}]$ cm s^{-1}M^{-1}	Sedimentation order (b) at constant $[M^{2+}]$	Sedimentation constant (ks_2) at constant $[M^{2+}]$ cm s^{-1}M^{-1}	Calculated (overall) rate constant (ks_T) cm s^{-1}M^{-2}
SrCO$_3$	+0.21	1.01 x 10^{-1}	+0.35	1.36 x 10^{-1}	2.47 x 10^{-1}
BaCO$_3$	-0.67	2.32 x 10^{-3}	-1.01	3.81 x 10^{-4}	1.00 x 10^{-4}

Settling Characteristics of the Metal Carbonates: Two patterns of settling behaviour were observed; they illustrated the nature and size of the particles that make up the precipitates. In one, it was observed that settling started shortly after mixing and stirring were done. The settling was relatively rapid. The precipitates yield was small but the particles were relatively large. In the other, after mixing and initial stirring were undertaken, the precipitates remained stable without settling for an interval. To overcome these observed anomalies, each sedimentation measurement was run using a fresh mixture. It was also observed that the period of stability varied with the concentrations of both the metal ions and that of the precipitating agent. However, with further stirrings, this initial stability began to collapse, and the initial settling rates became appreciable. These precipitates were observed to have large number of small particles which were colloidal in nature.

Colloidal particles have large-surface-to-mass ratio, which promote surface adsorption (Gary, 2004). Brownian motion (Skoog, *et. al.*, 1995) and an equilibrium-based adsorption process, characteristic of colloidal particles, determined the initial rate of sedimentation of the precipitates. Equilibrium favoured the formation of larger particles. Surfaces of particles tended to adsorb the ions of the precipitate particles that were in excess in the solution. On the other hand, smaller particles tended to dissolve and reprecipitate on the surfaces of larger ones. This resulted in particle growth which, over time, began to settle as the constituent particles appreciated in size.

Sedimentation Rate Profiles of SrCO$_3$ and BaCO$_3$: The sedimentation plots in Figures 1 and 2 illustrate that whereas strontium carbonate precipitates showed increase in sedimentation rate with increase in concentrations of both strontium and carbonate ions; the reverse was the case for barium carbonate precipitates. These patterns illustrate the nature of the precipitates and the interactions that occur between the precipitate particles and the mother liquor. Although, strontium ions are smaller in size than barium ions and also strontium carbonate less

dense than barium carbonate (Lee, 1989 & SLAC, 2014), it was expected that the sedimentation rate of their precipitates would exhibit similar characteristics as was the case between magnesium carbonate and calcium carbonate (Obunwo*et. al.*, 2014). A close observation reveals that strontium carbonate precipitates are crystalline in nature while those of barium carbonate are colloidal. The colloidal nature of the barium carbonate precipitates apparently increased the tendency of the particles to participate in the "electrical double layer" effect which confers buoyancy on the precipitate particles. Furthermore, with increasing concentration of excess ions, as the barium ions concentrations were varied, in the mother liquor, the "electrical double layer" effect become more pronounced.
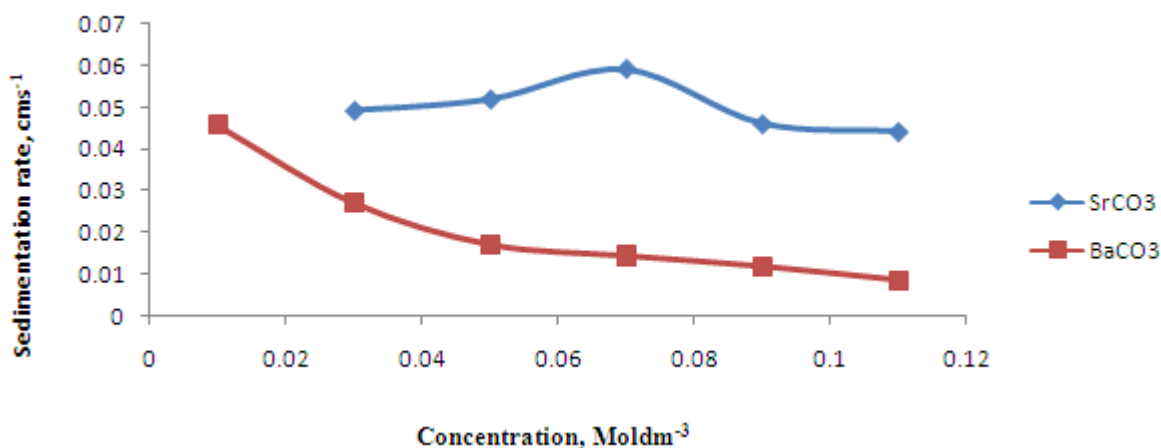

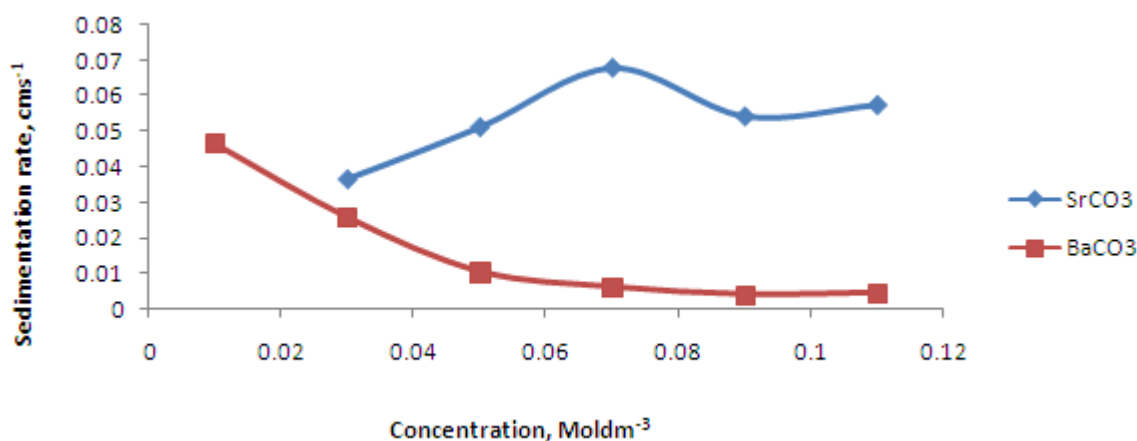**Figure 1:** Sedimentation rate profiles of $SrCO_3$ and $BaCO_3$, precipitates at constant $[CO_3^{2-}]$.

Figure 2: Sedimentation rate profiles of $SrCO_3$ and $BaCO_3$ precipitates at constant $[M^{2+}]$.

Sedimentation Rate Parameters: Results of the initial sedimentation rates are plotted against varying initial concentrations of metal ions (Figure 3) and varying initial concentrations of carbonate ions (Figure 4). Thesedimentation order and sedimentation rate constant for strontium carbonate at constant carbonate ions concentration were respectively 0.21 and 1.01×10^{-1} cm $s^{-1}M^{-1}$.

Although, settleable precipitates did not form (a cloudy solution mixture was observed) at a concentration of 0.01M, the second, third, and fourth initial concentrations showed a positive increase in sedimentation rate. However,at concentrations, 0.09M and 0.11M, a decrease in sedimentation rate was observed, due to particles supersaturation in the mother liquor. The highest sedimentation rate recorded was $0.0593cms^{-1}$ at 0.07M of strontium ions concentration.

Figure 1 shows that the sedimentation rates of $BaCO_3$ precipitates decreased with increase in concentration of barium ions, with the highest sedimentation rate of $0.0458cms^{-1}$ occurring at a barium ion concentration of 0.01M. The sedimentation order and sedimentation rate constant for barium carbonate precipitates at constant carbonate ions concentration (Table1) were respectively-0.67 and 2.32×10^{-3} cm $s^{-1}M^{-1}$.
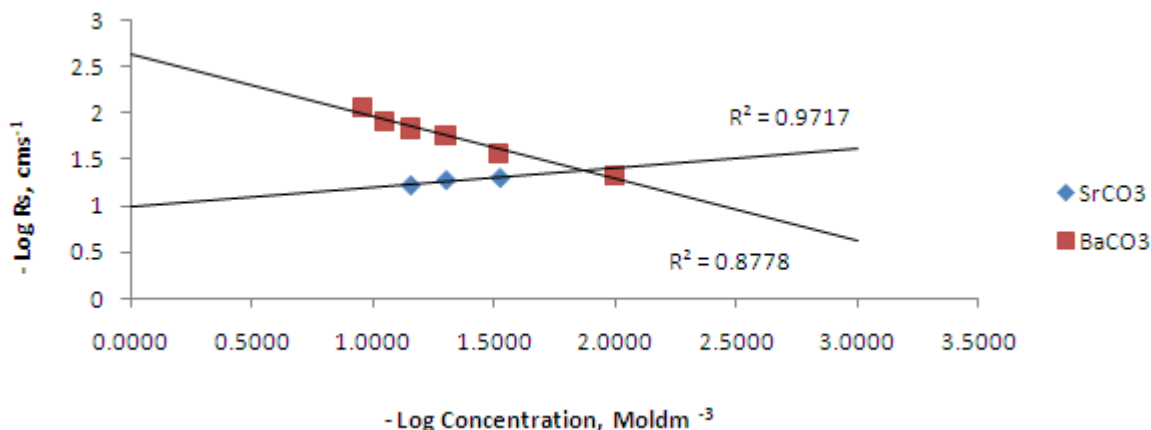
Figure 3: Sedimentation order plots of $SrCO_3$ and $BaCO_3$ at constant $[CO_3^{-2}]$.
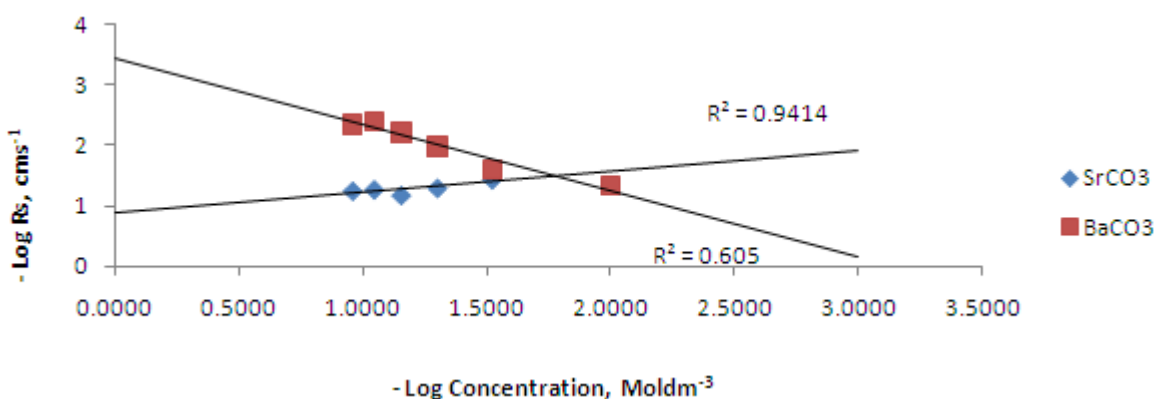

Figure 4: Sedimentation order plot of $SrCO_3$ and $BaCO_3$ at constant $[Mg^{2+}]$.

Atconstant strontium ions concentration, the sedimentation rates of $SrCO_3$ precipitates increased with increase in concentrations of the carbonate ions from 0.03M to 0.07M. However,a slight decrease was observed at 0.09M and 0.11M which might be due to particle supersaturation. The sedimentation order and sedimentation rate constant were, respectively 0.35 and 1.36 x 10^{-1} cm s^{-1}M^{-1}.

At constant barium ions concentration, the sedimentation rates of $BaCO_3$ precipitates decreased with increase in concentrations of carbonate ions. The sedimentation order and sedimentation rate constant values of -1.01 and 3.81 x 10^{-4} cm s^{-1}M^{-1}were obtained.

From Figures 1 and 2, it can be inferred that the initial sedimentation rate of the carbonates studied were affected by concentration.
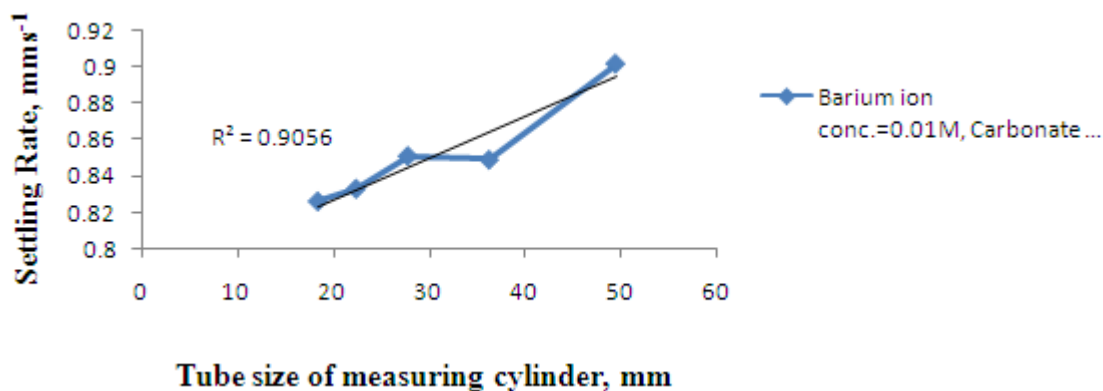

Figure 5: Correlation of gravitational settling rate as a function of internal diameter of measuring cylinder for $BaCO_3$ precipitates.

Sedimentation of BaCO₃ precipitates in cylinders: The settling process of $BaCO_3$ precipitates monitored under similar experimental conditions in various tubes with different sizes showed a positive increase in rate as the size of the tube was increased (Figure 5). A correlation coefficient of 90% was established. A similar observation was made by Lowell and Rose (1991) when they measured sediment-particles settling velocity in various diameters of a modified bottom withdrawal tube.

IV.   Conclusion

We have studied the effect of reactant concentration on the sedimentation rate of $SrCO_3$ and $BaCO_3$ in chemical precipitation process. It was observed that colloidal size of barium carbonate precipitates enhanced their interaction with the mother liquor and this drastically reduced the precipitates sedimentation rate. On the other hand, $SrCO_3$ produced crystalline precipitates with no observable particle-medium interactions, hence had increased sedimentation rate. Gravitational sedimentation study of precipitates in measuring cylinders of various sizes showed a positive increase in settling rate when the sizes of settling vessels were increased. Wall effect (Christie, 2003), pressure gradient, particle shape/crystal structure, and ion-ion/ion-solvent interactions may have contributed to the difference in settling rate in different sized settling vessels.

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