

Evaluation of the Effects of Temperature and Ion Concentration Variables on Sedimentation of Magnesium and Barium Phosphates in Aqueous Media

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Abstract

Abstract: Sedimentation studies have the possibility of providing profile curves and other vital parameters useful for modeling two-phase flow operations and dimensioning of clarification tanks in water purification plants. In continuation of the study on sedimentation of alkaline-earth metal phosphates, the effects of temperature and ion concentration variables on sedimentation rate profiles, order and rate constant of trimagnesium phosphate (TMP) and tribarium phosphate (TBP) precipitates were evaluated at different temperatures using the Modified Isolation (Initial Rate) method. It was found that, for TMP precipitate, initial sedimentation was dependent on temperature variations at high concentrations of magnesium and phosphate ions. On the other hand, it was dependent on temperature at low concentrations (0.02M) of barium and phosphate ions, for TBP precipitate. TMP precipitate content in reaction vessel decreased as temperature of the medium and concentrations of magnesium and phosphate ions mixed were increased. For TBP, precipitate content in reaction vessel increased as temperature of the medium and concentrations of barium and phosphate ions mixed were increased. These results suggest that, although temperature and ion concentration influence sedimentation of precipitate, ion concentration is probably more influential than temperature especially when precipitate content in reaction vessel is high.

Key Words: trimagnesium phosphate, tribarium phosphate, temperature, ion concentration, sedimentation properties, precipitate

1.0 INTRODUCTION

Bench-scale sedimentation studies have the possibility of providing clarifying profile curves and other important parameters required to design clarifiers and thickeners for use in waste water treatment plants as well as modeling two-phase flow operations [1, 2]. Contrary to traditional sedimentation process involving settling of solid materials introduced into stationary columns by operators, there are, however, precipitate sedimentation processes involving settling out of solid phase materials formed from solution medium. Applications abound in chemical pre-treatment processes such as in water and sewage treatment and in analytical separations where flocculating and precipitating agents are added to aqueous suspensions to effect precipitation and subsequent sedimentation of insoluble particles [3]. Experimental study of precipitate sedimentation can be realized in settling apparatus such as graduated transparent cylinder [4]. Conditions (temperature, concentration, stirring, pH) can be adjusted to either enhance or hinder the process [5].

Solubility product data from Sapling, SLAC [6, 7] indicate magnesium and barium form strong phosphate precipitates that may settle out spontaneously in their suspensions, if left to stand. Recently, Obunwo *et al.* [8] reported the influence of temperature and ion concentration on sedimentation characteristics of tricalcium and tristrontium phosphates precipitates. The study provided profiles and other parameters useful for describing gravitational sedimentation behaviours of calcium and strontium phosphates. In this companion study, the effects of temperature and ion concentration variables on sedimentation rate profile and other properties (order, rate constant) of trimagnesium phosphate (TMP) and tribarium phosphate (TBP) precipitates were evaluated, using the Modified Isolation Method. The objective was to present the effects of temperature and ion concentration on

sedimentation profiles and properties of TMP and TBP precipitates. Data may serve as models for correction of temperature and concentration variations in sedimentation process.

2.0 MATERIALS AND METHODS

Solutions containing magnesium, barium and phosphate ions were separately prepared using analytical grade magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$), barium nitrate ($Ba(NO_3)_2$) and tribasic sodium phosphate (Na_3PO_4) and de-ionized water.

Precipitate sedimentation measurement apparatus was set up using a transparent cylindrical tube (with graduated scale on the outside), Pec Medical Magnetic Stirrer Hotplate (Model Number: 85-2), transparent 3000cm³ capacity beaker (as water-bath), thermometer, magnetic stirrer, and clamp and stand. The transparent cylindrical tube is the main item in which precipitate sedimentation measurement was done. Graduation on the outside of the tube enabled the displacement of the precipitate to be read visually. The magnetic stirrer hotplate provided controlled heat to the sample (in the tube) through the water in the water-bath. The desired heat supply to the sample was maintained by adjusting temperature control knobs on the magnetic stirrer hotplate. To ensure uniform distribution of heat to the sample (precipitate), the magnetic stirrer was positioned to stir the water in the water-bath without disturbing the sample and the process while the thermometer reads the temperature of the water. The clamp and stand held the cylindrical tube into the water-bath. Other items were a light source and digital stop clock. The light source (5.5 watts LED rechargeable desk lamp) was placed behind the water-bath to illuminate the cylindrical tube for visual monitoring. The digital stop clock was used for taking timely readings of the precipitate sedimentation tests.

The Modified Isolation (Initial Rate) Method, involving turn-wise variation and isolation of reactant concentration and measurement of initial sedimentation rate [2, 9, 10], was employed. Tests were performed by mixing known volume (40ml) of varying concentrations (0.2M - 1.0M) of magnesium ions or (0.02M - 0.1M) of barium ions with constant 0.6M or 0.06M phosphate ions concentration, respectively, to form either trimagnesium phosphate (TMP), $Mg_3(PO_4)_2$, or tribarium phosphate (TBP), $Ba_3(PO_4)_2$, precipitate. Accordingly, the process was repeated by varying the concentration of phosphate ions while keeping the concentration of magnesium or barium ions constant. TMP precipitate [$Mg_3(PO_4)_2$] did not form when low concentrations (0.02M - 0.10M) of magnesium and phosphate ions were mixed. Precipitate formed when a 9-fold increase in concentration range (0.2M - 1.0M) relative to the original range (0.02M - 0.10M), designed for the study, was mixed. In each test, the precipitate suspension formed after mixing was stirred immediately for 30 seconds and then allowed to stand. The displacement (H) of the suspension front was monitored and the corresponding time (T) recorded every 30 seconds, for 150 seconds. The rate, at which the suspension zone moved, in the early stages, was used to obtain the initial sedimentation rates, R_s , (Equation 1). In precipitates exhibiting low sedimentation, for example $Mg_3(PO_4)_2$, the appearance of the suspension interface marked the onset of sedimentation and the time the interface formed was also used to measure the initial sedimentation rate (R_s). The tests were conducted at different temperature settings (30°C, 35°C, 40°C, 45°C, 50°C and 55°C) of the sedimentation measurement apparatus.

The sedimentation behaviour of insoluble material (precipitate) from solution medium depends upon the concentrations of reacting species [8, 11]. Hence, sedimentation rate, R_s , was expressed with respect to the concentrations of the metal (Equation 2) and phosphate (Equation 3) ions. Plots of $\log(R_s)$ against $\log(\text{ion species})$ determined other sedimentation parameters.

$$R_s = \frac{H}{T} = \frac{-(hp_i - hp_0)}{t_i - t_0} \quad (1)$$

$$R_{sM} = K_{sM} [M^{2+}]^a \quad (2)$$

$$R_{sP} = K_{sP} [P^{3-}]^b \quad (3)$$

Where: hp_i = height of the precipitate suspension at a given time, t_i , hp_0 = height of the suspension at time zero, t_0 , R_s = Initial sedimentation rate, R_{sM} and R_{sP} = Sedimentation rates with respect to metal (M) and phosphate (P) ions, K_{sM} and K_{sP} = Sedimentation rate constants with respect to metal (M) and phosphate (P) ions (a) and (b) = sedimentation orders with respect to metal (M) and phosphate (P) ions, and M = Magnesium or barium.

3.0 RESULTS AND DISCUSSION

3.1 Sedimentation Rate Profiles of TMP and TBP precipitates at Various Temperatures: Initial sedimentation rate results of TMP and TBP precipitates are displayed in Figures 1, 2, 3 and 4 as function of temperature for various concentrations of the metal (magnesium and barium) and phosphate ions. Results in Figures 1 and 2 show that initial sedimentation rate of TMP precipitate is dependent on temperature variations when solutions containing high concentrations of magnesium and phosphate

ions were mixed. TMP sedimentation profiles corresponding to 0.4M, 0.6M, 0.8M and 1.0M magnesium ion concentrations, given in Figures 1 and 2, show positive increases in initial sedimentation rate as temperature rose from 30 to 55°C. A near zero increase was observed for the 0.2M magnesium ions concentration. Similarly, profiles for 0.6M, 0.8M and 1.0M gave positive correlated TMP initial sedimentation rate when phosphate ions concentration was varied. Slightly negative and near zero correlations were obtained for 0.2M and 0.4M phosphate ions concentrations. For TBP, the results in Figures 3 and 4 show that initial sedimentation rate of TBP precipitate was influenced by temperature at low concentrations (0.02M) of barium and phosphate ions. Rise in temperature from 30 to 55°C produced positively correlated initial sedimentation rate profiles for 0.02M barium and phosphate ions concentrations. Profiles corresponding to 0.04M, 0.06M, 0.08M and 0.10M barium and phosphate ions concentrations generally gave near zero correlation. Figures 1 and 2 also indicate that, at higher temperatures, concentrations of magnesium and phosphate ions mixed influenced initial sedimentation rate of resulting TMP precipitate. For example, at 45°C initial sedimentation rate of TMP precipitate increased from 0.0023 to 0.0037cms⁻¹, 0.0037 to 0.0125cms⁻¹, 0.0125 to 0.0119cms⁻¹, and 0.0119 to 0.0133cms⁻¹ when magnesium ions concentration increased from 0.2 to 0.4M, 0.4 to 0.6M, 0.6 to 0.8M and from 0.8 to 1.0M. Similarly, when phosphate ions concentration was increased from 0.2 to 0.4M, 0.4 to 0.6M, 0.6 to 0.8M and from 0.8 to 1.0M, TMP precipitate initial sedimentation rate respectively rose from 0.0005 to 0.0010cms⁻¹, 0.0010 to 0.0014cms⁻¹, 0.0014 to 0.0025cms⁻¹ and 0.0025 to 0.0033cms⁻¹. For TBP, Figures 3 and 4 show that initial sedimentation rate of TBP precipitate was influenced by low concentrations (<0.04M) of barium and phosphate ions mixed. For example, at 35°C initial sedimentation rate of TBP precipitate dropped from 0.1544 to 0.1539cms⁻¹ and 0.1572 to 0.1556cms⁻¹ when the barium and phosphate ions concentrations were respectively increased from 0.02 to 0.04M. When barium and phosphate ions concentrations increased from 0.04 to 0.06M, TBP initial sedimentation rate decreased further from 0.1539 to 0.1533cms⁻¹ and 0.1556 to 0.1522cms⁻¹, respectively.

The appearance of TMP precipitate suspension varied along temperature and concentration lines. It was observed that TMP precipitate suspension mixture gradually changed into paste-like sticky gel as temperature was raised from 30°C to 55°C. Also, the cloudiness of the suspension decreased as the concentration of magnesium or phosphate ions in mixture increased. No rate result was recorded for 0.2M phosphate ions concentration at 50°C. Again, no TMP precipitate initial sedimentation rate result was recorded for 0.2M, 0.4M and 0.6M phosphate ions concentrations at 55°C. It was observed that TMP precipitate suspension formed at these temperatures and concentrations were highly viscous and thick with no evidence of sedimentation even when allowed to stand beyond the early stages. Although, the cause of the decrease in cloudiness with increasing magnesium or phosphate ions concentration is not very clear, but may be due to gradual dissolution of the precipitate in the medium because of the high concentrations of magnesium and phosphate ions solutions mixed. Therefore, the combined effects of decreasing viscosity as temperature was raised and low precipitate content as concentrations of magnesium and phosphate ions mixed were increased were responsible for the observed increase in TMP precipitate initial sedimentation rate. In direct contrast to that of TMP, TBP precipitate content, as seen in the reaction vessel, increased with increase in concentration of barium and phosphate ions mixed. Suspension interface occurred in the upper and lower regions. For both variations (barium and phosphate ions), the suspension interface of the 0.02M concentrations were observed at the upper region and the precipitate formed was gelatinous in nature. A lower interface of more coarse TBP precipitate was observed from 0.04 to 0.10M barium and phosphate ions concentrations. This may represent a concentration-dependent transition from a colloidal size TBP precipitate to a more crystalline one.

Ideally, temperature and ion concentration affect sedimentation when considered separately, via change in medium viscosity [12]. It is a fact that at higher medium temperature, viscosity drops; hence decreased resistance of particles to settle, and an increase in sedimentation results [13]. Also, solutions of high reactant ions concentration, when mixed, may result in high medium viscosity (increased inter-particle interactions and resistance) if concentration of precipitate particles formed in reaction vessel is high. However, when temperature and concentration of solution of reactants ions are varied concurrently, the resultant event will depend on the magnitude of the contribution of each variable to the sedimentation process. At low reactants ion concentration (low precipitate content) and high medium temperature, decrease of viscosity may out-weigh interactions, thus initial sedimentation rate increases. At high reactants concentrations (high precipitate content) and medium temperature, inter-particle interactions out-weigh decrease of viscosity, and initial sedimentation rate decreases. These eventualities probably determined the outcomes.

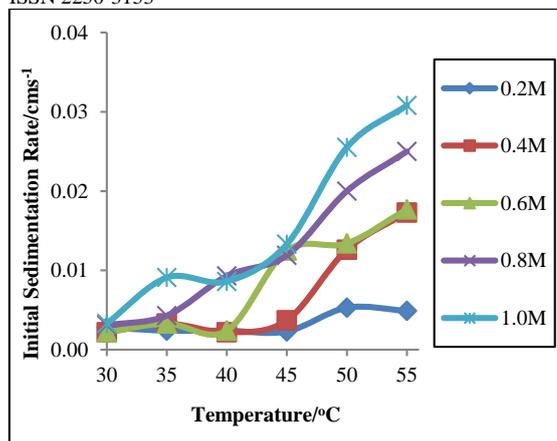


Figure 1: Initial sedimentation rate profiles of TMP precipitate as function of temperature for various $[Mg^{2+}]$.

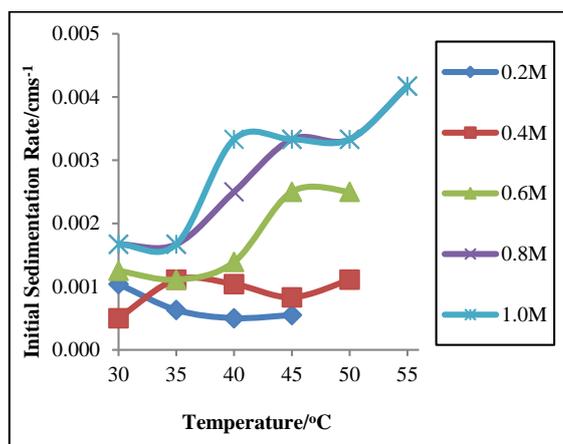


Figure 2: Initial sedimentation rate profiles of TMP precipitate as function of temperature for various $[PO_4^{3-}]$.

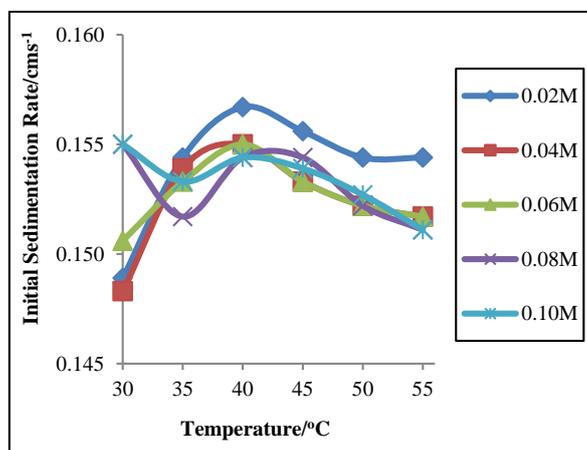


Figure 3: Initial sedimentation rate profiles of TBP precipitate as function of temperature for various $[Ba^{2+}]$.

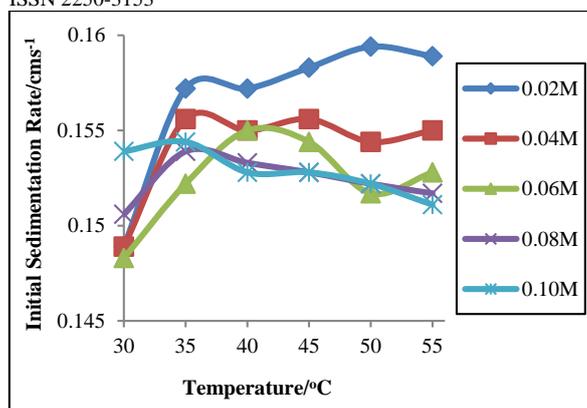


Figure 4: Initial sedimentation rate profiles of TBP precipitate as function of temperature for various $[PO_4^{3-}]$.

3.2 Kinetics of TMP and TBP Precipitates Sedimentation: Based on model similarity and perfect fit with the method of Initial Rate, primary sedimentation data were analyzed using the derived pseudo rate order laws (Equations 2 and 3). Tables 1 and 2 show additional sedimentation properties (order and rate constant) of TMP and TBP precipitates obtained at various temperatures. For TMP precipitate, sedimentation order ranged from 0.11 to 1.20 and -0.006 to 0.029 , for TBP, at constant phosphate ion concentration. At constant metal ion concentration, sedimentation order ranged from 0.45 to 1.27, for TMP, and -0.014 to 0.016 for TBP. Ranges of sedimentation rate constants (Ks) were also obtained. Sedimentation rate constant varied between 2.88×10^{-3} - 3.30×10^{-2} when phosphate ions concentration was kept constant and between 1.51×10^{-3} - 3.93×10^{-3} at constant magnesium ions concentration. For TBP precipitate, it varied between 1.46×10^{-1} - 1.65×10^{-1} when phosphate ions concentration was kept constant and between 1.41×10^{-1} - 1.57×10^{-1} when barium ions concentration was kept constant. Closer look at Tables 1 and 2 shows that sedimentation orders and rate constants of TMP precipitate vary slightly with temperature whereas those of TBP precipitate do not. Although, the reason for this is not obvious, but may have been due to the fact that temperature markedly influenced the sedimentation of TMP precipitate but poorly affected that of TBP. Also, particle-medium interactions, stronger in TMP suspension than TBP, may be responsible for the variation. The order and rate constant of sedimentation do not provide much information about the sedimentation process. Nevertheless, by extrapolation, rate constant of sedimentation equates measured gravitational sedimentation rate at infinite dilution. Values of the sedimentation rate constant also depend on the size of the precipitate particles formed. High sedimentation rate constant is obtained when precipitate formed tends to be crystalline and low when precipitate formed tends to be colloidal.

Table 1: Influence of Temperature on Sedimentation Parameters of TMP Precipitate.

Temperature, °C	Sedimentation Order (a) at constant $[PO_4^{3-}]$	Sedimentation Rate Constant, k_{SMg} , at constant $[PO_4^{3-}]$, ($cms^{-1}M$)	Sedimentation Order (b) at constant $[Mg^{2+}]$	Sedimentation Rate Constant, k_{SP} , at constant $[Mg^{2+}]$, ($cms^{-1}M$)
30	0.11	2.88×10^{-3}	0.45	1.51×10^{-3}
35	0.67	6.18×10^{-3}	0.61	1.74×10^{-3}
40	0.87	7.13×10^{-3}	1.16	3.05×10^{-3}
45	1.20	1.54×10^{-2}	1.27	3.80×10^{-3}
50	0.93	2.48×10^{-2}	1.24	3.93×10^{-3}
55	1.08	3.30×10^{-2}	**	**

** Incomplete data due to formation of stable TMP precipitate suspension below 0.6M phosphate ions concentration.

Table 2: Influence of Temperature on Sedimentation Parameters of TBP Precipitate.

Temperature, °C	Sedimentation Order (a) at constant $[PO_4^{3-}]$	Sedimentation Rate Constant, k_{SBa} , at constant $[PO_4^{3-}]$, ($cms^{-1}M$)	Sedimentation Order (b) at constant $[Ba^{2+}]$	Sedimentation Rate Constant, k_{SP} , at constant $[Ba^{2+}]$, ($cms^{-1}M$)
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30	0.029	1.65×10^{-1}	0.016	1.57×10^{-1}
35	-0.008	1.50×10^{-1}	-0.014	1.48×10^{-1}
40	-0.010	1.51×10^{-1}	-0.017	1.47×10^{-1}
45	-0.006	1.52×10^{-1}	-0.023	1.45×10^{-1}
50	-0.007	1.50×10^{-1}	-0.030	1.41×10^{-1}
55	-0.013	1.46×10^{-1}	-0.032	1.46×10^{-1}

CONCLUSION

The effects of temperature and ion concentration on initial sedimentation rates of trimagnesium phosphate (TMP) and tribarium phosphate (TBP) precipitates were determined using the Modified Isolation (Initial Rate) Method. It was found that, for TMP precipitate, initial sedimentation was dependent on temperature variations at high concentrations of magnesium and phosphate ions; it was dependent on temperature at low concentrations (0.02M) of barium and phosphate ions, for TBP precipitate. TMP precipitate content in reaction vessel decreased as temperature of the medium and concentrations of magnesium and phosphate ions mixed were increased. For TBP, precipitate content in reaction vessel increased as temperature of the medium and concentrations of barium and phosphate ions mixed increased. Sedimentation data obtained in this study fitted well the pseudo rate order law, implying the dependence of initial sedimentation rate on ion concentration. Whereas TMP precipitate produced positive sedimentation order, TBP precipitate gave negative order. Data may serve as models for correction of temperature and concentration variations in precipitate sedimentation process.

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