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Studies on the effect of temperature on the sedimentation of insoluble metal carbonates

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ABSTRACT: The effect of temperature on the sedimentation rate of some insoluble metal carbonates has been investigated in this work. The sedimentation constants show that a 20°C rise in temperature typically doubles the rate of sedimentation. Cadmium carbonates have higher sedimentation constants while nickel had the lowest sedimentation constants. The order of sedimentation does not seem to have any dependence on temperature. The minimum energy needed to activate the sedimentation process was higher for Zn^{2+}, 67.90kJmol^{-1} and lowest for Ni^{2+}, 25.5kJmol^{-1}. The dependence of the metal carbonates on temperature follows the order $Zn^{2+} > Cd^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+}$. @JASEM

Sedimentation is the settling out of solid particles (sediments) in a liquid by gravity (Atkin, 1994). Chemical sediments represent precipitation of materials in solution either by simple chemical precipitation or by the activity of organisms (Fisher, 1997). Sedimentation readily occurs when particle size is above 1000nm. Particles below 1000nm exist as colloids in solution (Shaw, 1992). There are many chemical reactions that form solid deposits (precipitates). Precipitation is the process that produces a separable solid phase within a liquid medium (Vemulapalli, 1993). The free settling of the precipitates under gravity can be monitored to determine sedimentation rates, sedimentation constants and sedimentation orders of the insoluble compounds. These parameters have been determined for the insoluble transition metal hydroxides (Essien, 1992) and cobalt(II) insoluble compounds (Essien and Ekpe, 1998). Sedimentation studies have been used to determine the molecular weights of protein (Lustig *et al*, 2000).

In continuation of our work on sedimentation (Mkpenie and Onwu, 2006), we examine the effects of temperature on the sedimentation of insoluble transition metal carbonates. This study may provide models for correction of temperature variation on sedimentation parameters.

EXPERIMENTAL

All chemicals used were of analytical grade.

Procedure

The experimental procedure was similar to the one used elsewhere (Mkpenie and Onwu, 2006). 20 ml of the precipitating agents (0.1M Na_2CO_3) was gently added to 20ml of the metal ions (0.01-0.2 M) in a 100 ml measuring cylinder, stirred and allowed to stand. The time taken for the precipitates to fall was recorded at various volumes along the measuring cylinder. This was carried out at different temperatures, 8°C, 21°C, 28°C and 50°C. The rate of sedimentation was obtained from the slope of the plot of the change in volume of the sedimenting carbonates (ΔV) against time (t). The precipitated carbonates were obtained as expressed in equation (1) and the rate of sedimentation was obtained according to equation (2).

$$M^{2+} + CO_3^{\ 2-} \Leftrightarrow MCO_3^{\ 2-} \qquad (1)$$

$$R_S = \frac{k_S}{[M^{n+}]^a} \qquad (2)$$

where

R_S is the sedimentation rate

k_S is the sedimentation rate constants = $k/[A]^b$

$[M^{n+}]$ is the concentration of the metal ion

a and b are sedimentation orders

The sedimentation constant k_S was deduced from the intercept of the plot of log R_S versus log $[M^{n+}]$ while the sedimentation order was deduced from the slope. The variation of sedimentation with temperature was determined by Arrhenius plot, Ink_S versus 1/T.

RESULTS AND DISCUSSION

The sedimentation rates of some transition metal carbonates were determined under the influence of gravity. Variation of sedimentation parameters with temperature is shown in table 1. The rate of sedimentation has been found to follow Arrhenius equation as in chemical reactions. Zn^{2+} has higher sedimentation rates while nickel has lower sedimentation rates. The rates at all temperatures seem to follow the order $Zn^{2+} > Cd^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+}$. The sedimentation order shows no dependence on temperature. Ni^{2+} has second order of sedimentation, Zn^{2+} and Co^{2+} have first order while that of Cu^{2+} and Cd^{2+} may be 3/2 and 1/2 respectively.

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Arrhenius equation predicts that a small increase in temperature will produce a marked increase in the magnitude of the rate constants. The rate of sedimentation typically doubles for a 20°C rise in temperature. At higher temperatures (>50°C), sedimentation becomes difficult. This is due to increase in solubility of the carbonates.

Table 1: Variation of Sedimentation Parameters with Temperature.

M^{n+}	Temperature (°C)	Sedimentation Order	Sedimentation Constant (k_S x 10^{-4} s^{-1})	Sedimentation Rate (R_S x 10^{-2} s^{-1})	Activation Energy (Ea $kJmol^{-1}$)
	8	1.31	1.58	0.53	
	21	1.41	3.46	1.14	
Zn^{2+}	28	1.43	14.12	5.10	67.90
	50	1.00	60.26	6.90	
	8	0.63	1.43	0.52	
	21	0.59	2.94	0.92	
Cd^{2+}	28	0.86	5.76	3.65	52.30
	50	0.63	24.50	4.17	
	8	1.54	1.38	0.51	
	21	1.52	2.51	0.62	
Cu^{2+}	28	1.51	3.55	0.85	31.20
	50	1.42	7.76	2.04	
	8	0.98	1.26	0.16	
	21	1.10	1.86	0.20	
Co^{2+}	28	1.19	2.45	1.28	30.20
	50	1.24	6.61	0.71	
	8	1.70	0.08	0.05	
	21	1.77	0.11	0.07	
Ni^{2+}	28	1.76	0.16	0.11	25.50
	50	2.03	0.32	0.15	

The sedimentation activation energy for Zn^{2+} was higher (67.9$kJmol^{-1}$) while that of Ni^{2+} was lower. (25.5$kJmol^{-1}$). This may represent the minimum energy required for sedimentation to occur and may involve mostly the energy of interaction of the precipitates with the liquid medium. Reactions with small activation energy (about 10$kJmol^{-1}$) have rates that increase only slightly with temperature whereas reactions with large activation energy (about 60$kJmol^{-1}$) have rates that depend strongly on temperature (Atkins, 1989) (Figure 1). Thus, sedimentation rates in Zn^{2+} depends strongly on temperature. The dependence of metal carbonates on temperature follows the order: Zn^{2+} > Cd^{2+} >Cu^{2+} > Co^{2+} > Ni^{2+}.

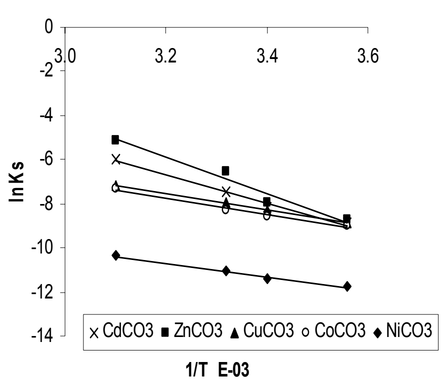

Fig. 1: Variation of Sedimentation Rates with Temperature

In conclusion, sedimentation, being a physical phenomenon has shown much resemblance to chemical processes and follows Arrhenius-type behaviour. There is a general increase in the rate of sedimentation with temperature. A 20°C rise in temperature typically doubles the rate of sedimentation. The order of sedimentation is independent of temperature.

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