

Periodic crystallisation of magnesium hydroxide in agar-agar gel. Influence of temperature

S AMBROSE, F D GNANAM and P RAMASAMY*

A. C. College of Technology, Anna University, Madras 600 025, India.

MS received 23 October 1982

Abstract. The influence of temperature on periodic crystallisation of magnesium hydroxide in agar-agar gel has been studied. The increase in velocity constant with temperature is attributed to the increase in the diffusion constant with temperature. The activation energy for diffusion of aqueous ammonia is calculated from the temperature - velocity constant correlation. The solubility of $Mg(OH)_2$ decreases with temperature. The decrease in the spacing coefficient and flocculation value of $Mg(OH)_2$ with temperature is also explained because of the increase in temperature. Matalon and Packter's equation correlating the spacing coefficient and concentration of the inner electrolyte is suitably modified to satisfy the temperature dependence of the spacing coefficient.

Keywords. Periodic crystallisation; magnesium hydroxide; agar-agar gel; velocity constant; spacing coefficient; activation energy; flocculation value.

1. Introduction

Under suitable conditions, precipitates formed by counter diffusion of reacting solutions in gels or other porous media may be deposited in a number of bands or layers separated by void spaces. This phenomenon could result in concentric configuration. Since it was first observed by Liesegang (1897) many investigators have studied its various aspects and applications.

Liesegang rings are reminiscent of certain structures found in nature *e.g.*, the striations of agate, malachites, manganese nodules, the stripes on tigers and zebras, bladder-stones, etc. Close relationship between radial configuration in rocks, minerals and rhythmic depositions has been observed and this phenomenon has important applications in geology (Hatschek and Simon 1912; Richardson 1921) and biology (Kuester 1918).

Geologists explain the structures in agates as a rhythmic precipitation of iron compound (Liesegang 1926) in the original SiO_2 jelly. The internal growth features of some ores reveal that many nodules are structurally, chemically and mineralogical non-uniform. These ores are supposed to have originated by rhythmic precipitation. The origin of periodicity in nodules can therefore be investigated by periodic crystallisation. An understanding of the origin of nodules will facilitate the development and processing of ores of various kinds.

*To whom all correspondence should be made.

The occurrence of such banded or stratified structures in both organic and inorganic natural products are also explained assuming periodic supply of one or both components or a periodicity in external conditions like temperature (Hatschek 1922). The influence of the nature, ageing and pH of the gel medium (Matalon and Packter 1955) to the nature of the additives (Gnanam *et al* 1980) and the dependence of these factors on this phenomenon have all been studied earlier. Agates, manganese nodules and other ore deposits having stratified structures are found inside the earth and their origin depends upon the temperature. Some reports on the influence of temperature are already available (Popp 1925; Wentzy 1971; Schaaffs and Hawn 1974).

The periodic crystallisation of magnesium hydroxide and the effect of additives and gel on periodic crystallisation of magnesium hydroxide have been studied earlier (Ambrose *et al* 1982). The influence of temperature of the gel on the periodic crystallisation of magnesium hydroxide has now been investigated.

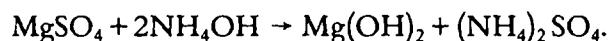
2. Experimental

2.1 Velocity constant and spacing coefficient

Hot agar-agar sol (40 ml and 1% by wt), the concentration impregnated with magnesium sulphate solution of molarity 0.041, 0.081, 0.122, 0.162 and 0.203 are taken in five different test tubes kept in a constant temperature bath maintained at 25°C. After the gel set, 10 ml of aqueous ammonia of concentration 14.68 M is taken over the gel. The gel contains a few drops of phenolphthaline indicator. As aqueous ammonia diffuses into the gel, the gel appears pink in colour. Thus the diffusion front is represented by the surface of demarcation. The position of the diffusion front is noted at different time intervals upto 140 hr. When the diffusion is complete, the position of the different banded precipitates from the gel boundary is measured with a cathetometer. The velocity constant and the spacing coefficient are calculated. The experiment is repeated for the same concentrations of the reactants and the gel, at different temperatures upto 43°C. Figures 1 and 2 show the dependence of the velocity constant and the spacing coefficient on temperature.

2.2 Solubility of magnesium hydroxide

Magnesium hydroxide is prepared as the precipitate by reacting magnesium sulphate with aqueous ammonia following the chemical equation



Magnesium sulphate ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$) (49.3 g) is dissolved in 200 ml of distilled water to get 0.2 M of magnesium sulphate solution. Aqueous ammonia (27.2 ml) of concentration 25% (14.68 M) is adjusted to 200 ml with distilled water to get aqueous ammonia of molarity 0.4. The two are gradually mixed to

get magnesium hydroxide precipitate is washed with distilled water and separated by suction filtration. $\text{Mg}(\text{OH})_2$ precipitate is kept in an oven at 120° for more than 7 hr. The dried precipitate is taken out and powdered and then used as the sample to determine solubility.

Distilled water (50 ml) taken in a test tube and added with 500 mg of magnesium hydroxide from the prepared sample is stirred well and kept in a constant temperature bath maintained at 25°C . Two sets of such samples are kept in constant temperature bath for 3 days and then taken out and the magnesium hydroxide solution in both samples filtered carefully by suction filtration. The solubility of magnesium hydroxide is determined by EDTA titration, (Belcher *et al* 1970). In this process Erio T indicator and pH 10 buffer solution are used. The experiment is carried out from 25 to 45°C . The solubility is observed to decrease with temperature.

3. Theory

3.1 Velocity constant and the activation energy for diffusion

When a hypertonic electrolyte diffuses into a gel charged with another hypotonic electrolyte, the advancing diffusion front obeys a general law (Morse and Pierce 1907)

$$x = 2 D^{1/2} \xi t^{1/2}, \quad (1)$$

where x is the position of the diffusion front from the gel boundary at t sec., D is the diffusion constant of the diffusing electrolyte and ξ is a constant. A rearrangement of the above equation gives,

$$\begin{aligned} x/t^{1/2} &= 2 D^{1/2} \xi, \\ K &= 2 D^{1/2} \xi, \end{aligned} \quad (2)$$

K being known as the velocity constant equal to $x/t^{1/2}$.

The diffusion constant is a function of temperature (Jost 1960)

$$D = D(T) = D_0 \exp(-E/kT), \quad (3)$$

where E is the activation energy for diffusion and k is the Boltzmann's constant. Incorporating (3) in (2)

$$\begin{aligned} K &= 2D_0^{1/2} \exp(-E/2kT) \xi, \\ K &= K_0 \exp(-E/2kT), \end{aligned}$$

where $K_0 = 2D_0^{1/2} \xi$,

and $\ln K = \ln K_0 - E/2kT$. (5)

Thus we observe a linear relationship between $\ln K$ and $1/T$, the slope being $(E/2k)$.

3.2 Spacing coefficient

Using Ostwald's supersaturation theory, Wagner (1950) has analysed the spacing coefficient. According to him,

$$p - 1 = H/\gamma^2 [k_s/C_{20}^{(v_1 + v_2)(2v_1 + v_2)}] \quad (6)$$

where C_{20} is the initial concentration of the hypotonic reagent, v_1 and v_2 are the valencies of the ions I_1 and I_2 forming the insoluble precipitate $[(I_1)_{v_2}(I_2)_{v_1}]$, H and γ are constants and k_s is the supersaturation product, otherwise called the solubility product. Equation (6) can be rearranged as

$$p - 1 = B/C_{20} \quad (7)$$

B is a constant dependent on the supersaturation product.

In studying the Liesegang phenomenon with reference to the sol protection and diffusion, Matalon and Packter (1955) have modified the Wagner's relationship in (7) as

$$p - 1 = \nu C_g^{m+\nu} B/C_{20} \quad (8)$$

In the above expression ν and m are arbitrary constants and C_g is the concentration of the gel.

3.3 Flocculation value

According to the revised coagulation theory (Shinohara 1970), the sol front is first formed due to the interaction between the diffusing hypertonic reactant and the impregnated hypotonic reactant. The sol front flocculates due to the ionic concentration contributed by the diffusing electrolyte and the parasitic electrolyte set free at the formation of the sol front. This is possible only when the ionic concentration reaches a value characteristic of the sol, called the flocculation value F .

Shinohara rearranged the diffusion equation as

$$\frac{sq \exp(-k^2/2)}{G(k)} = \frac{\exp(-k^2 s^2/2)}{[\frac{1}{2} - G(ks)]} \quad (9)$$

where $q = C_{10}/C_{20}$, $s = (D_{10}/D_{20})^{1/2}$.

C_{10} , C_{20} are the concentrations and D_{10} , D_{20} are the diffusion constants at the infinite dilution of the outer and inner electrolytes calculated from the Nernst equation (Perry 1963).

Using (9), the front constant k is computed. $k_1 = k/p$ where p is the spacing coefficient.

$$G(k) = \frac{1}{(2\pi)^{1/2}} \int_0^k \exp(-\eta^2/2) d\eta \quad (10)$$

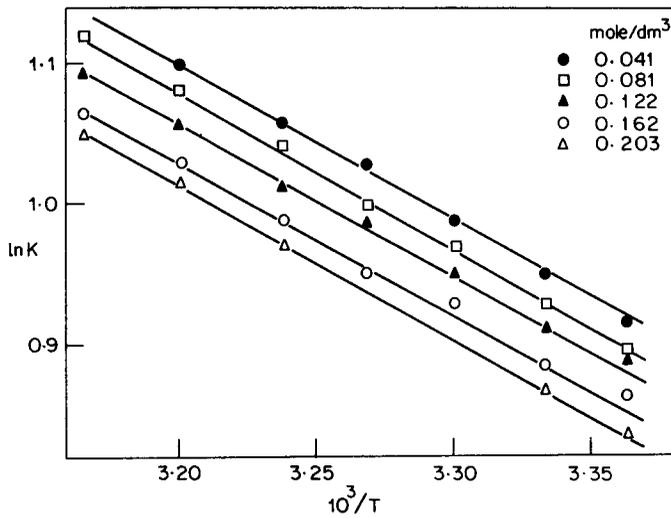


Figure 1. $\ln K$ vs temperature, for the concentration of the outer electrolyte (C_{10}) 14.68 mole/dm³ at different concentrations of the inner electrolyte.

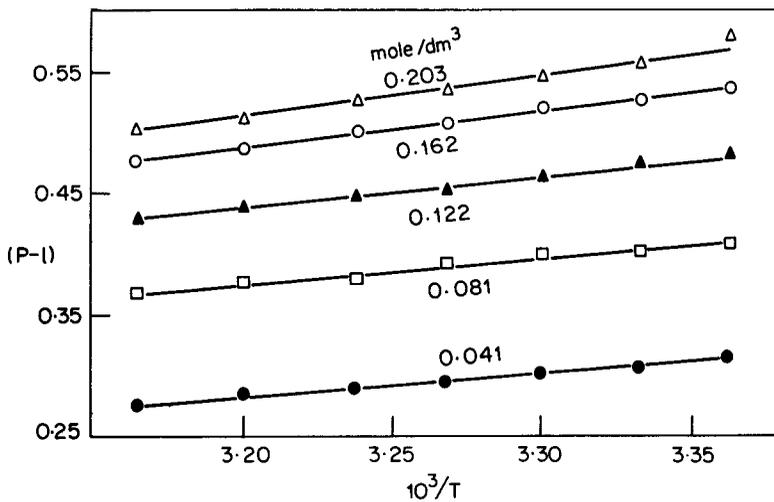


Figure 2. Spacing coefficient vs temperature, for the outer electrolyte concentration (C_{10}) 14.68 mole/dm³ at different concentrations of the inner electrolyte.

$$= C_{10} \left\{ \frac{G(k) - G(k_1)}{G(k)} \right\} \tag{11}$$

If C_{30} is the concentration of the supersaturated solution prior to sol formation.

$$C_{30} = \frac{C_{10} \exp(-k^2/2)}{(2\pi)^{1/2} k G(k)} \tag{12}$$

the flocculation value $F = \Gamma + C_{30}$ (13)

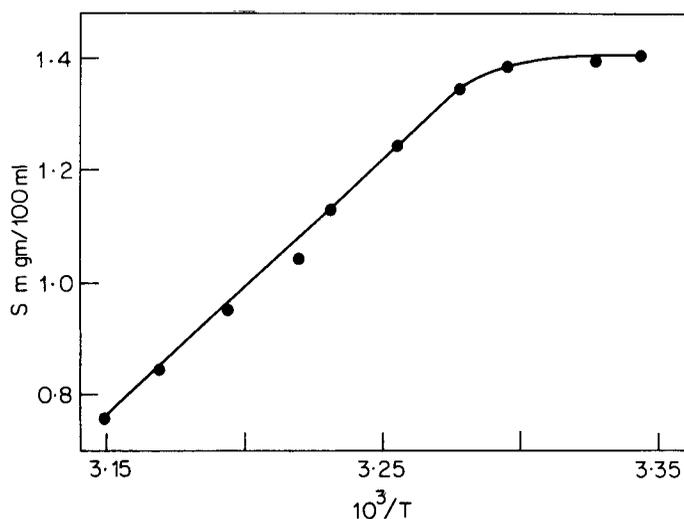


Figure 3. Solubility (S) vs temperature.

4. Discussion

4.1 Velocity constant and activation energy

The results obtained for the dependence of $\ln K$ on the reciprocal of the absolute temperature of the gel, are represented in figure 1. The straight line obtained is of negative slope and this agrees with the conclusion derived from (5). The velocity constant of the system mainly depends on the diffusion constant of the outer electrolyte, when the other conditions like the concentration of the reactants and the nature of the gel are the same. From (3) we find that the diffusion constant increases with the temperature. This leads to increase in the velocity constant with temperature of the gel. The results shown in figure 1 agree with the expected type of curve from (3). We also observe from (5) that the activation energy for diffusion (E) can be determined from the slope of the ($\ln K$ versus $1/T$) graph. The activation energy for diffusion of aqueous ammonia is found to be 0.1837 eV.

4.2 Spacing coefficient and solubility

The dependence of the spacing coefficient on temperature represented in figure 2 shows that the spacing coefficient decreases with the temperature of the gel. From (6) we find that the spacing coefficient has a linear relationship with k_s , the solubility product, which further depends on the solubility of the precipitate formed. Moreover Wagner has reported "when different precipitation reactions with equal values of ν_1 and ν_2 and equal initial concentrations are compared with each other the characteristic ratio ($p - 1$) is expected to be less, the lower the solubility of the salt formed by the reaction between the ions I_1 and I_2 ". Thus when the solubility of the reaction product is low, the

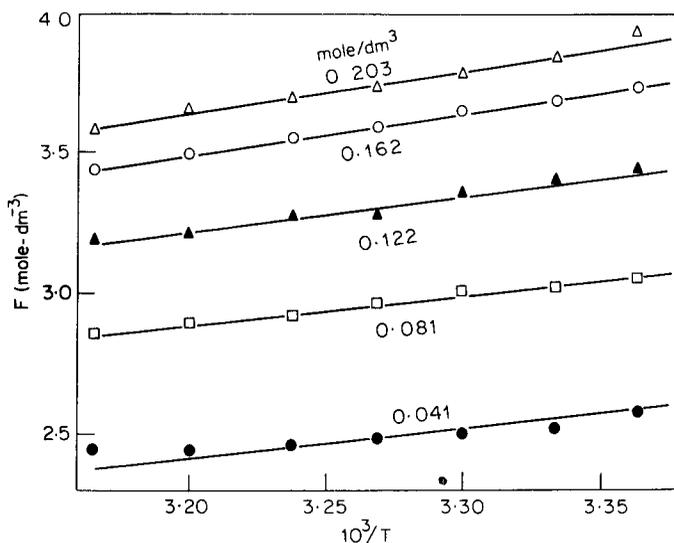


Figure 4. Flocculation value (F) vs temperature for the outer electrolyte concentration (C_{10}) 14.68 mole/dm³ at different concentrations of the inner electrolyte.

metastable solution of the reaction product will reach the ionic product required for flocculation much earlier and hence the precipitate is formed at closer distances leading to smaller values for the spacing coefficient.

A scan of literature reveals contradictory results regarding the variation of the solubility of $Mg(OH)_2$ with temperature. Weast (1981) reports that solubility of $Mg(OH)_2$ increases with temperature while the reported values for the same (Seidell 1940) reveal that the solubility of $Mg(OH)_2$ decreases with increase of temperature. Hence the solubility of $Mg(OH)_2$ was determined at different temperatures as explained in § 2.2. The normalised values at different temperatures represented in figure 3 show that the solubility of $Mg(OH)_2$ decreases with increase of temperature.

As the temperature of the gel increases, the metastable solution of magnesium hydroxide will reach the required critical ionic product quickly because of the decrease in the solubility. So the banded precipitates are formed at closer distances resulting in decrease in the spacing coefficient of magnesium hydroxide with increase of temperature.

From the modified equation of Matalon and Packter we find that when the concentration of the gel (C_g) and that of the inner reactant (C_{20}) are constant, $(p-1)$ is constant. γ is a constant independent of temperature whereas B is a constant dependent on supersaturation and hence on temperature. In other words $B = B(T)$ and (8) can be modified as

$$(p-1) = \gamma \frac{C_g^m + B(T)}{C_{20}} \quad (14)$$

Since the concentration of the gel (C_g) and that of the inner electrolyte are

Table 1. Solubility of magnesium hydroxide at different temperatures.

| Temperature °C | Solubility mg/100 ml |
|-------------------|-------------------------|
| 35 | 0.9857 |
| 45 | 0.8749 |
| 70 - 75 | 0.6883 |
| 100 | 0.4199 |

constant, the above equation can be rewritten as,

$$(p - 1) = A_1 + B_1/T \quad (15)$$

where A_1 and B_1 are constants. Figure 2 satisfies the above equation.

4.3 Flocculation value

Figure 4 represents the dependence of the flocculation value on the temperature of the reacting medium. We observe that the flocculation value decreases with temperature. As seen from figure 3, the solubility of $Mg(OH)_2$ decreases with temperature. So at higher temperature of the gel, the supersaturation product is lowered. Hence a smaller ionic concentration is sufficient to flocculate the metastable solution of the reaction product as the temperature of the gel is increased. Thus the flocculation value decreases with temperature confirming the experimental results.

5. Conclusion

The velocity constant of magnesium hydroxide thus increases with temperature of the gel. Studies on dependence of the velocity constant on temperature give the activation energy for diffusion of aqueous ammonia as 0.1837 eV. The spacing coefficient of magnesium hydroxide decreases with temperature of the gel, owing to the decrease in the solubility of magnesium hydroxide with temperature and this agrees with the result derived from Wagner's equation. It is experimentally found that the solubility of magnesium hydroxide decreases with temperature. The above result also accounts for the decrease in the flocculation value with temperature. Matalon and Packter's equation is also suitably modified to account for the linear relationship between the spacing coefficient and the reciprocal and the absolute temperature of the gel.

References

- Ambrose S, Kanniah N, Gnanam F D and Ramasamy P 1982 *Cryst. Res. Technol.* **17** 299, 609
 Atherton Seidell 1940 *Solubilities of inorganic and metal organic compounds* (New York: D Van Nostrand Company Inc.) 3rd edn. Vol 1 p. 982
 Belcher R, Nutten A J and Macdonald A M G 1970 *Quantitative Inorganic Analysis* (London: Butterworths) 3rd edn. p. 269

- Gnanam F D, Krishnan S, Ramasamy P and Laddha G S 1980 *J. Colloid Interface Sci.* **73** 193
- Hatschek E and Simon A L 1912 *Trans. Inst. Met.* **21** 451
- Hatschek E 1922 *Introduction to Physics and Chemistry of Colloids* (London: J & A Churchill) 4th edn. p. 118
- Jost W 1960 *Diffusion in Solids, Liquids & Gases* (New York: Academic Press) 3rd edn. p.468
- Kuster E 1918 *Beitr. Z. entwicklunge mechanischen anatomie der pflanzen*, heft 1 uber Zonen bildung, Jena
- Liesegang R E 1897 *Z. Phys. Chem.* **23** 365
- Liesegang R E 1926 *Colloid Chemistry* (ed) J Alexander (New York: Reinhold Pub. Corporation) Vol. 1, p. 788
- Matalon R and Packter A 1955 *J. Colloid Interface Sci.* **10** 46
- Morse H. W and Pierce G W 1903 *Phys. Chem.* **45** 589
- Perry J H (ed) 1963 *Chemical Engineers hand book* (New York: Mc Graw Hill Book Co) 4th edn p. 14
- Popp K 1925 *Kolloid Z.* **36** 208
- Richardson W A 1919 *Geol. Mag.* **56** 535
- Richardson W A 1921a *Trans. Inst. Min. Eng.* **60** 337
- Richardson W A 1921b *Mineral Mag.* **19** 96
- Schaffs W and Hawn L 1974 *Colloid Polym. Sci.* **252** 538
- Shinohara S 1970 *J. Phys. Soc. Jpn.* **29** 1073
- Wagner C 1950 *J. Colloid Interface Sci.* **5** 85
- Weast R C (ed) 1981 *CRC handbook of Chemistry and Physics* (Florida: CRC Press) 61st edn p. 116
- Wentzy J 1971 *Proc. S. Dak. Acad. Sci.* **50** 293