Chapter 5. PERIODIC CRYSTALLISATION OF MAGNESIUM HYDROXIDE IN AGAR AGAR GEL: INFLUENCE OF THE ADDITIVES.

5.1. Introduction.
5.2. Theory
5.3. Experimental verification.
5.3.1. Experimental
5.3.2. Result
5.3.3. Discussion.
5.4. Conclusion.
5.1. **Introduction:**

After the first observation of the periodic precipitation by Liesegang (1), a large number of investigators have examined this phenomenon for a wide range of insoluble materials, since there is a close similarity between this phenomenon and geological (2-4) and biological (5, 6) stratifications. Veil (7, 8) has presented a comprehensive range of substances which exhibit rhythmicity and stratification in gel media. There are experimental evidences that many factors such as nature and ageing of the gel influence the periodic crystallisation of the various sparingly soluble substances (9-11).

The role of additives on periodic crystallisation in gel has been studied by different investigators. Riegel and Reinhard (12) have found that the trace of chloride is necessary for the periodic crystallisation of silver chromate in gelatin. Matalon and Packter (13) have also studied the influence of additives on the silver chromate system. Hillson (14) have studied the role of water soluble impurities of low molecular weight on the periodic crystallisation. Buzagh and Fraknoy (15, 16) have studied the influence of electrolyte and non electrolyte impurities on calcium carbonate. Quanam et al (9) and Krishnan et al (17) have also studied the same for calcium carbonate. Kanniah et al (18) have studied the
effect of additives on the periodic crystallisation of cobalt (II) oxinate.

Many investigators have developed theories concerning the periodic precipitation. The earlier theories explain the phenomenon either on the basis of supersaturation (19-21) or coagulation of the sol (22). They take into account the diffusion of the reactants towards one another in the presence of imposed concentration gradient. Theories have been formulated on the mechanism of periodic precipitation based on the onset of chemical instability of the autocatalytic reactions in the absence of imposed concentration gradients (23-25). A mathematical formulation of Ostwald's supersaturation principle has been given recently taking into account the counter diffusion of the reactants and the diffusion of the reaction product assuming a reversible chemical reaction of the diffusing electrolytes (26). All these theories quantitatively explain the periodic crystallisation in general, but no theories have predicted the quantitative relationship of the additive concentration with the spacing coefficient and the velocity constant in the periodic precipitation of sparingly soluble substances in gels.

Klueh and Mullins (27) have observed periodic precipitation in solid silver and they have derived expressions for
the spacing coefficient in solid silver using Wagner's mathematical analysis. Van Hooijen et al (28) have predicted a theory on Liesegang bands in internally oxidised ternary alloys in which they expressed band spacing as a function of temperature and concentration of third element in the alloy. The author has explained quantitatively the effect of additives on periodic crystallisation of magnesium hydroxide (30).

In this chapter, the author discusses in detail, the quantitative explanation and the experimental verification of the same with reference to magnesium hydroxide.

5.2. Theory:

When an electrolyte diffuses into a gel charged with another electrolyte, according to Ostwald's supersaturation principle (31), precipitation occurs at positions where the ionic product exceeds a critical value corresponding to supersaturation product.

When the gel is impregnated with the inner reactant and the outer electrolyte diffuses into the gel, reaction product is formed. This reaction product advances as a single reaction front. The presence of an additive along with the inner reactant gives rise to two reaction fronts. Assuming
that the inner reactant and the additive have unequal affinity, one reaction front should appear first. If the additive has greater affinity it forms the first reaction front. This was experimentally observed in the present system.

An electrolyte of concentration $C_{20}$ is impregnated into a gel and another electrolyte of concentration $C_{10}$ is allowed to diffuse. When $C_{10} > C_{20}$, the hypertonic electrolyte diffuses into the other. The chemical reaction of the two leads to the precipitation of the sparingly soluble salt $(P, Q)$ where $P$ and $Q$ are the ions supplied by the outer and inner reactants, $\gamma_1$ and $\gamma_2$ being their stoichiometric values. Further an additive of concentration $C_{a0}$ supplying the ions of type $A$ is also present in the gel along with the inner reactant. The additive concentration is chosen to be very small compared to the concentrations of the reactants. $D_1$, $D_2$ and $D_a$ are the diffusion coefficients of the outer electrolyte, inner electrolyte and the additive.

When the ions of species $P$ react with the ions of species $Q$, the following equation holds good

$$\gamma_2 P + \gamma_1 Q \rightleftharpoons P\gamma_2 Q\gamma_1$$

the reaction rate $r$ at equilibrium is a function of the molar
concentrations $C_1(x,t)$, $C_2(x,t)$ and $C_M(x,t)$ of $P$, $Q$ and $M$, where $M$ is the reaction product $[P]_2 \cdot [Q]_1$. If the reaction is of the orders $\gamma_2$ in $P$, $\gamma_1$ in $Q$ and $\gamma_3$ in $M$, the law of mass action yields,

$$r = k_+ C_1^{\gamma_2} C_2^{\gamma_1} - k_- C_3^{\gamma_3} \tag{5.1}$$

Here $k_+$ and $k_-$ are the rate constants for the forward and backward reactions. In a similar manner the ions of species $P$ react with the additive ions of species $A$ following the equation,

$$\gamma_a P + \gamma_1 A \rightarrow \gamma_1 P_a A_1$$

For the reaction of the ions $P$ with the additive ions $A$,

$$r' = k_+ C_1^{\gamma_a} C_1^{\gamma_1} - k_- C_4^{\gamma_4} \tag{5.2}$$

where $r'$ is the reaction rate and $C_N$ is the concentration of the reaction product $[P]_a [A]_1$ represented as $N$. The reactions are of the orders $\gamma_a$ in $P$, $\gamma_1$ in $A$ and $\gamma'$ in $N$. $k_+$ and $k_-'$ are the rate constants for the forward and backward reactions.

Taking into account the reaction, the diffusion equations can be written as

$$\frac{\partial^2 C_1}{\partial t^2} = D_1 \frac{\partial^2 C_1}{\partial x^2} - \gamma_2 r - \gamma_3 r' \tag{5.3}$$
The above equations are called the reaction diffusion equations (26, 32). When the reaction is fast and reversible (33) then \( r = 0 \) and \( r' = 0 \). Moreover for small concentrations of the reacting electrolytes, Fick's equation can sufficiently represent the diffusion process (34). Thus eqns (5.3 - 5.5) reduce to the ordinary diffusion equations.

\[
\begin{align*}
\frac{\partial c_1}{\partial t} &= D_1 \frac{\partial^2 c_1}{\partial x^2} \quad \cdots \text{5.6} \\
\frac{\partial c_2}{\partial t} &= D_2 \frac{\partial^2 c_2}{\partial x^2} \quad \cdots \text{5.7} \\
\frac{\partial c'_a}{\partial t} &= D_a \frac{\partial^2 c'_a}{\partial x^2} \quad \cdots \text{5.8}
\end{align*}
\]

The boundary conditions are,

\[
\begin{align*}
C_1 &= C_{10} \quad \text{for } x < 0 \quad \cdots \text{5.9} \\
C_1 &= 0 \quad \text{for } x > 0 \quad \cdots \text{5.10} \\
C_2 &= C_{20} \quad \text{for } x > 0 \quad \cdots \text{5.11} \\
C_a &= C_{a0} \quad \text{for } x > 0 \quad \cdots \text{5.12} \\
C_1 &= C_{10} \quad \text{for } x = 0 \quad \cdots \text{5.13} \\
t > 0 & \quad C_2 = C_{20} \quad \text{for } x \rightarrow \infty \quad \cdots \text{5.14} \\
C_a &= C_{a0} \quad \text{for } x \rightarrow \infty \quad \cdots \text{5.15}
\end{align*}
\]
Very close to the layer formed by the ions of type P and Q, it is assumed that

\[ C_1 = C_1' \quad \text{and} \quad C_2 = C_2' \]  \hspace{1cm} \text{(5.16)}

such that

\[ [C_1']^{1/2} [C_2']^{1/2} = \prod_1 \]  \hspace{1cm} \text{(5.17)}

where \( \prod_1 \) is the solubility product of the precipitate M.

Very close to the layer formed by the ions of type P and A, it is assumed that

\[ C_1 = C_1'' \quad \text{and} \quad C_a = C_a' \]  \hspace{1cm} \text{(5.18)}

such that

\[ [C_1'']^{1/2} [C_a']^{1/2} = \prod_2 \]  \hspace{1cm} \text{(5.19)}

where \( \prod_2 \) is the solubility product of the precipitate N.

The reaction fronts are assumed to obey the condition,

\[ \frac{x_a}{2(D_1 t)^{1/2}} = \text{constant} \]

If \( x_2 \) and \( x_a \) are the distances of the two reaction fronts from the gel boundary after equal interval of time from the starting of the diffusion,

\[ x_2 = 2 \frac{1}{2} (D_1 t)^{1/2} \]  \hspace{1cm} \text{(5.20)}

\[ x_a = 2 \frac{1}{2} (D_a t)^{1/2} \]  \hspace{1cm} \text{(5.21)}
where $\xi_2$ and $\xi_a$ are constants. Further it is assumed that

$$s_2 = \frac{D_1}{D_2}^{1/2} \quad \ldots \text{5.22}$$

$$s_a = \frac{D_1}{D_a}^{1/2} \quad \ldots \text{5.23}$$

The solution of eqn. 5.6 is of the form

$$C_1 = A_1 + B_1 \text{erf} \frac{x}{2(D_1t)^{1/2}} \quad \ldots \text{5.24}$$

In the region $x < x_2$

Using the condition represented in eqn. 5.13, namely, $C_1 = C_{10}$ at $x = 0$ for $t > 0$, eqn. 5.24 can be written as

$$C_{10} = A_1$$

Using the condition represented in eqn. 5.16, viz. $C_1 = C_1'$ at $x = x_2$, eqn. 5.13 is written as

$$C_1' = A_1 + B_1 \text{erf} \xi_2$$

But $A_1 = C_{10}$

$$B_1 = -\frac{C_{10} - C_1'}{\text{erf} \xi_2}$$

Substituting the values of $A_1$ and $B_1$, eqn. 5.24 is written as

$$C_1 = C_{10} - \frac{(C_{10} - C_1')}{\text{erf} \xi_2} \text{erf} \frac{x}{2(D_1t)^{1/2}} \quad \ldots \text{5.25}$$
In the region $x > x_a$

Using the boundary condition represented by eqn. 5.10, namely $C_1 = 0$ at $t = 0$ and $x > 0$, eqn. 5.24 is written as,

$$0 = A_1 + B_1 \text{erf} a$$

$$A_1 = -B_1$$

Using the boundary condition represented by eqn. 5.18, namely $C_1 = C_1''$ when $x > x_a$, eqn. 5.24 is written as,

$$C_1'' = A_1 + B_1 \frac{x_a}{2(D_1 t)^{1/2}}$$

$$= -B_1 + B_1 \text{erf} \xi_a$$

$$C_1'' = -B_1 [1 - \text{erf} \xi_a]$$

$$B_1 = -\frac{C_1''}{1 - \text{erf} \xi_a}$$

$$A_1 = \frac{C_1''}{1 - \text{erf} \xi_a}$$

Substituting the values of $A_1$ and $B_1$ in eqn. 5.24,

$$C_1 = \frac{C_1''}{1 - \text{erf} \xi_a} - \frac{C_1''}{1 - \text{erf} \xi_a} \frac{x}{2(D_1 t)^{1/2}}$$

$$= \frac{C_1''}{1 - \text{erf} \xi_a} [1 - \text{erf} \frac{x}{2(D_1 t)^{1/2}}]$$

$$C_1'' \text{erfc} \frac{x}{2(D_1 t)^{1/2}}$$

$$C_1 = \frac{C_1''}{\text{erfc} \xi_a} \ldots 5.26$$
In the region $x_2 \leq x \leq x_a$

The boundary condition as represented in eqn. 5.16 is

$$C_1 = C_1' \text{ when } x = x_2.$$ Substituting in eqn. 5.24,

$$C_1' = A_1 + B_1 \text{ erf } \frac{x_2}{2(Dt)^{1/2}}$$

$$C_1' = A_1 + B_1 \text{ erf } \zeta_2 \quad .. 5.27$$

Substituting in eqn. 5.24 the boundary condition represented in eqn. 5.18,

$$C_1'' = A_1 + B_1 \text{ erf } \zeta_a$$

$$C_1'' = A_1 + B_1 \text{ erf } \zeta_a \quad .. 5.28$$

The values of $A_1$ and $B_1$ are found by solving eqns. 5.27 and 5.28.

$$A_1 = \frac{C_1' \text{ erf } \zeta_a - C_1'' \text{ erf } \zeta_2}{\text{ erf } \zeta_a - \text{ erf } \zeta_2} \quad .. 5.29$$

$$B_1 = \frac{C_1'' - C_1'}{\text{ erf } \zeta_a - \text{ erf } \zeta_2} \quad .. 5.30$$

Substituting the values of $A_1$ and $B_1$ in eqn. 5.24,

$$C_1 = \frac{C_1' \text{ erf } \zeta_a - C_1'' \text{ erf } \zeta_2}{\text{ erf } \zeta_a - \text{ erf } \zeta_2} + \frac{(C_1'' - C_1') \text{ erf } \frac{x}{2(Dt)^{1/2}}}{\text{ erf } \zeta_a - \text{ erf } \zeta_2}$$
Simplifying,

\[ C_1 = C_1' - \left( C_1' - C_1'' \right) \frac{(\text{erf} \frac{x}{2(D_1 t)^{1/4}} - \text{erf} \frac{x}{(D_1 t)^{1/4}})}{(\text{erf} \frac{x}{a} - \text{erf} \frac{x}{b})} \] .. 5.31

The general solution of eqn. 5.7 is of the form,

\[ C_2 = A_2 + B_2 \frac{x}{2(D_2 t)^{1/4}} \] .. 5.32

Using the boundary condition represented in eqn. 5.14, ie.

\[ C_2 = C_{20} \text{ when } x \to \infty \text{ for all } t, \]

\[ C_{20} = A_2 + B_2 \] .. 5.33

Using the boundary condition (eqn. 5.16),

\[ C_2' = A_2 + B_2 \frac{x}{2(D_2 t)^{1/4}} \]

\[ C_{20}' = A_2 + B_2 \frac{s_2}{s_2} \] .. 5.34

Solving eqns. 5.33 and 5.34, \( A_2 \) and \( B_2 \) are evaluated.

\[ B_2 = \frac{C_{20} - C_{20}'}{1 - \text{erf} \frac{x_s}{s_2}} \]

\[ A_2 = C_{20} - \frac{C_{20} - C_{20}'}{1 - \text{erf} \frac{x_s}{s_2}} \]

Substituting in eqn. 5.32,

\[ C_2 = C_{20} - \frac{C_{20} - C_{20}'}{1 - \text{erf} \frac{x_s}{s_2}} + \frac{C_{20} - C_{20}'}{1 - \text{erf} \frac{x_s}{s_2}} \frac{x}{2(D_2 t)^{1/4}} \]

\[ C_2 = C_{20} - \frac{C_{20} - C_{20}'}{\text{erfc} \frac{x_s}{s_2}} \frac{x}{2(D_2 t)^{1/4}} \] .. 5.35
The solution of eqn. 5.8 is of the form

\[ C_a = A + 3 \frac{\text{erf} - X}{2(D_a t)^{1/2}} \]  \[ \text{.. 5.36} \]

Using the initial boundary condition in eqn. 5.15 i.e.,
\[ C_a = C_{a0} \text{ when } x \rightarrow \infty \text{ for all } t, \]
\[ C_{a0} = A + B \]  \[ \text{.. 5.37} \]

Making use of the boundary condition given by eqn. 5.18,
\[ C_a' = A + B \frac{\text{erf} \frac{x}{a} s_a}{\text{.. 5.38}} \]

Eqns. 5.37 and 5.38 are solved to evaluate \(A\) and \(B\).

\[
B = \frac{C_{a0} - C_a'}{1 - \text{erf} \frac{x}{a} s_a}
\]

\[
A = C_{a0} - \frac{C_{a0} - C_a'}{1 - \text{erf} \frac{x}{a} s_a}
\]

Substituting the values of the constants \(A\) and \(B\) in eqn. 5.36,
\[
C_a = C_{a0} - \frac{C_{a0} - C_a'}{\text{erfc} \frac{x}{a} s_a} \frac{\text{erf} C - X}{2(D_a t)^{1/2}} \text{.. 5.39}
\]

The diffusing outer electrolyte supplies the ions \(P\) of valency \(\gamma_1\). The inner electrolyte and the additive supply ions \(Q\) and \(A\) of valencies \(\gamma_2\) and \(\gamma_a\). The formation of the reaction product \(M\) satisfies the following stoichiometric condition.
The rate at which the ions of species P arrive per unit area at $x_2$ is $\left(\frac{2}{3}\right)$ times the rate at which the ions of species Q are consumed per unit area at $x_2$.

The formation of the reaction product $N$ satisfies the following stoichiometric condition, namely, the rate at which the ions of species P arrive per unit area at $x_2$ is $\left(\frac{2}{3}\right)$ times the rate at which ions of species A are consumed per unit area at $x_2$.

Consider an element of the gel impregnated with ions of species P bounded by two layers of unit area of cross section at distances $(x_2 - \delta x)$ and $(x_2 + \delta x)$ above and below the reaction front at $x_2$. Since $C_1 > C_2$, the ions reaching $x_2$ from below are consumed in the chemical reaction with P. The rate at which the ions of species P enter per unit area of cross section of the element at $(x_2 - \delta x)$ is given by

$$- D \frac{\partial C_1}{\partial x} \bigg|_{x_2 - \delta x}$$

The rate at which the ions of species P leave per unit area of cross section of the element at $(x_2 + \delta x)$ is given by

$$- D \frac{\partial C_1}{\partial x} \bigg|_{x_2 + \delta x}$$
The net rate at which the ions of species \( P \) arrive per unit area of cross section of the element is given by

\[
\left. \frac{\partial}{\partial x} \right|_{x_2 - \delta x} + \left. \frac{\partial}{\partial x} \right|_{x_2 + \delta x} \frac{\partial C_1}{\partial x}
\]

The rate at which the ions of species \( P \) arrive per unit area at \( x_2 \) is given by

\[
\left. \frac{\partial}{\partial x} \right|_{x_2 - \delta x} \frac{\partial C_2}{\partial x}
\]

Since all the ions of species \( Q \) arriving at the element are consumed in the chemical reaction with \( P \), no ions leave the element. So, the net rate at which the ions of species \( Q \) arrive per unit area at \( x \) is given by

\[
\left. \frac{\partial}{\partial x} \right|_{x_2 + \delta x} \frac{\partial C_2}{\partial x}
\]

Making use of the stoichiometric condition for the formation of the reaction product \( M \), one gets

\[
\left. \frac{\partial}{\partial x} \right|_{x_2 - \delta x} - \left. \frac{\partial}{\partial x} \right|_{x_2 + \delta x} \frac{\partial C_1}{\partial x} = \frac{\partial C_2}{\partial x}
\]

.. 5.40
By a similar reasoning, making use of the stoichiometric condition for the formation of the reaction product, it can be written as,

\[ \frac{\partial C_1}{\partial x} \bigg|_{x_2 + \delta x} = \frac{\partial C_1}{\partial x} \bigg|_{x_2 - \delta x} = \left( \frac{\partial C}{\partial x} \bigg|_{x_2 + \delta x} \right) \delta x \rightarrow 0 D_a \frac{\partial C_a}{\partial x} \left( x_a + \delta x \right) \]

Differentiating eqn. 5.31, with respect to \( x \), one gets

\[ \frac{\partial C_1}{\partial x} = - \frac{[C_1' - C_1]}{\text{erf} \left( \frac{x_2}{L_1} \right) - \text{erf} \left( \frac{x_2}{L_2} \right)} \frac{1}{(\mu t \mu t)^{\frac{3}{2}}} \exp \left( - \frac{x^2}{4D_1 t} \right) \]

Differentiating eqn. 5.25 with respect to \( x \), one gets

\[ \frac{\partial C_1}{\partial x} = - \frac{[C_1' - C_1]}{\text{erf} \left( \frac{x_2}{L_1} \right) - \text{erf} \left( \frac{x_2}{L_2} \right)} \frac{1}{(\mu t \mu t)^3} \exp \left( - \frac{x^2}{4D_1 t} \right) \]

.. 5.42

.. 5.43
Differentiating eqn. 5.35 with respect to \( x \),

\[
\frac{\partial C_2}{\partial x} = \frac{(c_{20} - c_{21})}{\text{erfc} \left( \xi_2^{-2} \right)} \frac{1}{(\pi D_2 t)^{1/2}} \exp\left( -\frac{x^2}{4D_2 t} \right)
\]

\[
\frac{\partial C_2}{\partial x} \bigg|_{x=\delta x} = \frac{(c_{20} - c_{21})}{x_2+\delta x} \frac{1}{(\pi D_2 t)^{1/2}} \exp\left( -\frac{(x_2 + \delta x)^2}{4D_2 t} \right)
\]

Combining equations 5.40, 5.42, 5.43 and 5.44, one gets

\[
\left[ \frac{D_1 \beta}{\pi t} \right]^{1/2} \exp\left( -\frac{x_2^2}{4D_1 t} \right) \frac{c_{10} - c_{11}}{\text{erf} \left( \xi_2^{-2} \right)} - \frac{c_{11} - c_{11}'}{\text{erf} \left( \xi_a^{-2} \right) - \text{erf} \left( \xi_2^{-2} \right)} = \frac{\gamma_0}{\gamma_1} \frac{D_2}{D_1}^{1/2} \frac{c_{20} - c_{21}}{\text{erfc} \left( \xi_2^{-2} \right)} 
\]

Replacing \( \frac{x_2}{\sqrt{4D_1 t}} = \xi_2^{-2} \)

\[\frac{x_2^2}{4D_2 t} = \xi_2^{-2} s_2^{-2}\]

and further simplifying, eqn. 5.45 reduces to

\[
\frac{c_{10} - c_{11}}{\text{erf} \left( \xi_2^{-2} \right)} - \frac{c_{11} - c_{11}'}{\text{erf} \left( \xi_a^{-2} \right) - \text{erf} \left( \xi_2^{-2} \right)} = \frac{\gamma_0}{\gamma_1} \frac{(c_{20} - c_{21})}{\text{erfc} \left( \xi_2^{-2} s_2^{-2} \right)} 
\]

\[
\exp\left[ -\xi_2^{-2} (s_2^{-2} - 1) \right]
\]

.. 5.46
Differentiating eqn. 5.26 with respect to x,

\[
\frac{\partial C_1}{\partial x} = \frac{C_1''}{(1-\text{erf} \, \xi_a)} - \frac{1}{(\pi D_1 t)^{3/2}} \exp\left(-\frac{x^2}{4D_1 t}\right) 
\]

Differentiating eqn. 5.31 with respect to x

\[
\frac{\partial C_1}{\partial x} = \frac{(C_1' - C_1'')}{(\text{erf} \, \xi_a - \text{erf} \, \xi_2)} - \frac{1}{(\pi D_1 t)^{3/2}} \exp\left(-\frac{x^2}{4D_1 t}\right) 
\]

Differentiating eqn. 5.39 with respect to x, one gets,

\[
\frac{\partial C_a}{\partial x} = \frac{C_a - C_a'}{\text{erfc} \, \xi_a} - \frac{1}{(\pi D_a t)^{3/2}} \exp\left(-\frac{x^2}{4D_a t}\right) 
\]

Substituting in eqn. 5.41 the values from eqns. 5.47, 5.48 and 5.49, one gets
Using eqns. 5.52, 5.53 and 5.54 in eqn. 5.46, and simplifying, one gets

\[
\frac{C_{10} - C_1'}{2 \xi_2} - \frac{C_1' - C_1''}{2 (\xi_a - \xi_2)} = \frac{\gamma_2}{\gamma_1} \left( C_{20} - C_2' \right) \xi_2 \exp \frac{\xi_2^2}{4D_1t}
\]
Further assuming $C_1'' = 0$ and $\exp \xi_2^2 = 1$, 

$$\frac{C_{10} - C_1'}{\xi_2} - \frac{C_1'}{\xi_a - \xi_2} = 2 \frac{v_2}{v_1} (C_{20} - C_2') \xi_2 \quad \ldots \quad 5.55$$

Similarly using eqns. 5.52, 5.53 and 5.54 in 5.51, and further assuming that $C_a' = 0$ and $\exp \xi_a^2 = 1$, one gets 

$$\frac{C_1'}{\xi_a - \xi_2} = 2 \frac{v_a}{v_1} \xi_a C_a \quad \ldots \quad 5.56$$

It can be assumed that $\xi_2 \simeq \xi_a$. Hence in the R.H.S. of eqn. 5.56, $\xi_a$ can be replaced by $\xi_2$. Thus one gets, 

$$\frac{C_1'}{\xi_a - \xi_2} = 2 \frac{v_a}{v_1} \xi_a C_a \quad \ldots \quad 5.57$$

From eqn. 5.17, 

$$C_1' = \frac{\prod 1/v_2}{[C_2']} \quad \ldots \quad 5.58$$

$$C_2' = \frac{\prod 1/v_1}{[C_1']} \quad \ldots \quad 5.59$$

Combining eqns. 5.57 and 5.59, 

$$C_2' = \frac{\prod 1/v_1}{[2 \frac{v_a}{v_1} (\xi_a - \xi_2) \xi_2 C_a]} \frac{v_2/v_1}{\ldots \quad 5.60}$$
Rearranging eqn. 5.55

\[
\frac{C_{10} - C_{1'}}{\xi_2} = \frac{C_{1}'}{\xi_a - \xi_2} + 2(\frac{\gamma_2}{\gamma_1}) \xi_2 (C_{20} - C_{2'})
\]

\[
= \frac{C_{1}'}{\xi_a - \xi_2} \left[ 1 + 2 \frac{\gamma_2}{\gamma_1} \frac{2(C_{20} - C_{2'})}{c_1'} (\xi_a - \xi_2) \right]
\]

From eqn. 5.57, \(C_{1}' = 2(\frac{\gamma_a}{\gamma_1}) (\xi_a - \xi_2) \xi_2 c_{a0}\)

\[
\frac{C_{10} - C_{1'}}{\xi_2} = \frac{C_{1}'}{(\xi_a - \xi_2)} \left[ 1 + \frac{\gamma_2 (C_{20} - C_{2'})}{\gamma_a c_{a0}} \right]
\]

Using eqn. 5.56,

\[
\frac{C_{1}'}{\xi_a - \xi_2} = 2 \frac{\gamma_a}{\gamma_1} \xi_a c_{a0}
\]

\[
\frac{C_{10} - C_{1'}}{\xi_2} = 2 \frac{\gamma_a}{\gamma_1} \xi_a c_{a0} \left[ 1 + \frac{\gamma_2 (C_{20} - C_{2'})}{\gamma_a c_{a0}} \right]
\]

Further simplification leads to

\[
\frac{C_{10} - C_{1'}}{\xi_2} = \frac{2 \xi_a}{\gamma_1} [\gamma_a c_{a0} + \gamma_2 (C_{20} - C_{2'})]
\]

\[
\xi_2 \xi_a = \frac{\gamma_1 (C_{10} - C_{1'})}{2 [\gamma_a c_{a0} + \gamma_2 (C_{20} - C_{2'})]}
\]

Assuming \(\xi_2 \approx \xi_a\)
\[ c_2 = \left[ \frac{\gamma_1 (C_{10} - C_{1'})}{2[\gamma_a C_{a0} + \gamma_2 (C_{20} - C_{2'})]} \right]^{1/2} \] .. 5.61

Substituting \( \frac{x_2}{t^{1/2}} = K \), the velocity constant, in eqn. 5.20, one gets

\[ c_2 = \frac{K}{2D_1 t^{1/2}} \]

Substituting the value of \( c_2 \) in eqn. 5.61,

\[ K = \left[ \frac{2D_1 \gamma_1 (C_{10} - C_{1'})}{\gamma_a C_{a0} + \gamma_2 (C_{20} - C_{2'})} \right]^{1/2} \] .. 5.62

Eqn. 5.62 represents the velocity constant of the diffusing electrolyte for different additive concentrations in the gel.

The product of the concentrations of the two ions can be calculated at any point around \( x_4 \). If at some point \( x = x_m \), this product exceeds the supersaturation product, precipitation occurs. If this condition is maintained continuously, continuous precipitation will be observed. On the other hand, if it is maintained only periodically, periodic precipitation will be formed. Assuming that the next band is formed at \( x_m \) while the reaction front coincides with \( x_2 \), the position of the previous band, \((x_m - x_2)\) is taken as the distance between successive bands.
Calculations are further simplified by linearising the concentrations $C_1(x)$ and $C_2(x)$. Assuming $C_1'' = 0$ and using the approximations $\text{erf} = \frac{2}{\sqrt{\pi} t^{3/2}} x$, eqn. 5.31 can be rewritten as

$$C_1(x) = C_1' - \frac{x}{2(\mu_1 t)^{3/2}} \frac{\xi_2}{(\xi_1 - \xi_2)}$$

.. 5.62a

Using eqns. 5.20 and 5.21 in eqn. 5.62a

$$C_1(x) = C_1' \frac{(x_a - x)}{(x_a - x_2)}$$

.. 5.63

In the region $x_2 < x < x_a$, the concentration $C_2(x)$ can be written as,

$$C_2(x) = C_2' + \left( \frac{2 C_2}{2} \right) \frac{1}{(x - x_2)}$$

.. 5.64

Differentiating eqn. 5.35,

$$\frac{\partial C_2}{\partial x} \bigg|_{x=x_2} = \frac{(C_{20} - C_2') \exp[-\frac{x_2^2}{4D_2 t}]}{\pi D_2 t^{3/2}} \text{erfc} \frac{\xi_2 s_2}{\xi_2 s_2}$$

.. 5.65

Replacing $\frac{x_2}{\sqrt{4D_2 t}} = \xi_2 s_2$ and $t^{1/2} = \frac{x_2}{2 \xi_2 s_2}$, eqn. 5.65 reduces to,
\[
\frac{\partial C_2}{\partial x^2} \bigg|_{x=x_2} = \frac{2}{\pi^{1/2}} \frac{(C_{20} - C_{2'})^2 s_2^2 \exp(-\frac{x^2}{2 s_2^2})}{x_2 \text{erfc}\left(\frac{x}{\sqrt{2} s_2}\right)}
\]

Combining eqns. 5.64 and 5.66, one gets

\[
C_2(x) = C_2' + \frac{\phi}{x_2} \quad \ldots \quad 5.67
\]

In the above equation, \(\phi\) is a constant independent of \(x_2\)

\[
\phi = \frac{2}{\pi^{1/2}} \frac{(C_{20} - C_{2'})^2 s_2^2}{x_2^2} \frac{\exp(-\frac{x^2}{2 s_2^2})}{\text{erfc}\left(\frac{x}{\sqrt{2} s_2}\right)} \quad \ldots \quad 5.68
\]

Using the approximation

\[
\text{erfc}\ x = -\frac{1}{\pi^{1/2}} \frac{\exp(-x^2)}{x}
\]

eqn. 5.68 reduces to

\[
\phi = 2 \frac{s_2^2}{\gamma_2} (C_{20} - C_{2'}) \quad \ldots \quad 5.69
\]

\[
\left[ \begin{array}{c}
\frac{1}{x} C_1(x) = C_1(x) C_2(x)
\end{array} \right] \quad \ldots \quad 5.70
\]

Substituting the values of \(C_1(x)\) and \(C_2(x)\) in eqn. 5.70 using eqns. 5.63 and 5.67,

\[
\left[ \begin{array}{c}
\frac{1}{x} C_1(x) = C_1'(\frac{x_a - x}{x_a - x_2}) \left[ C_2' + \frac{\phi}{x_2} \frac{(x - x_2)\text{erfc}\left(\frac{x}{\sqrt{2} s_2}\right)}{x_2}\right]
\end{array} \right] \quad \ldots \quad 5.71
\]

Differentiating with respect to \(x\)

\[
\frac{\partial}{\partial x} \left[ \begin{array}{c}
\frac{1}{x} C_1'(x_a - x) \phi - \frac{C_1'}{(x_a - x_2)^2} \left[ C_2' + \frac{\phi(x - x_2)\text{erfc}\left(\frac{x}{\sqrt{2} s_2}\right)}{x_2}\right]
\end{array} \right] \quad \ldots \quad 5.71
\]
Making use of the condition that $\frac{\partial \eta}{\partial x} = 0$ at $x = x_m$
in eqn. 5.71, one gets

$$C_2' + \phi \frac{x_m - x_2}{x_2} = (x_a - x_m) \frac{\phi}{x_2}$$

Further simplification leads to,

$$x_m = \frac{(x_a + x_2)}{2} - \frac{C_2' x_2}{2\phi} \quad \ldots 5.72$$

The spacing coefficient $p = \frac{x_m}{x_2}$

$$p = \frac{(x_a + x_2)}{2x_2} - \frac{C_2'}{2\phi}$$

$$= \frac{1}{2} + \frac{x_a}{2x_2} - \frac{C_2'}{2\phi}$$

$$(p-1) = \frac{x_a}{2x_2} - \frac{1}{2} - \frac{C_2'}{2\phi}$$

$$p-1 = \frac{1}{2} \left[ \frac{(x_a - x_2)}{x_2} - \frac{C_2'}{\phi} \right] \quad \ldots 5.73$$

From eqns. 5.20 and 5.21

$$p-1 = \frac{1}{2} \left[ \frac{x_a - x_2}{x_2} - \frac{C_2'}{\phi} \right]$$

$$p-1 = \frac{1}{2} \frac{(x_a - x_2)}{x_2} \left\{ 1 - \frac{C_2'}{\phi \left( x_a - x_2 \right)} \right\} \quad \ldots 5.74$$
From eqn. 5.57,
\[ \begin{align*}
\frac{C_{10} - C_1'}{\xi_2} &= \frac{C_{1}'}{\xi_a - \xi_2} \left\{ \frac{\gamma_a C_{a0} + \gamma_2 (C_{20} - C_2')}{\gamma_a C_{a0}} \right\} \\
\frac{\xi_3 - \xi_2}{\xi_2} &= \frac{C_{1}'}{C_{10} - C_1'} \left\{ \frac{\gamma_a C_{a0} + \gamma_2 (C_{20} - C_2')}{\gamma_a C_{a0}} \right\}
\end{align*} \]

Substituting in eqn. 5.74,
\[ p-1 = \frac{1}{2} \left( \frac{C_{1}'}{(C_{10} - C_1')} \right) \left\{ \frac{\gamma_a C_{a0} + \gamma_2 (C_{20} - C_2')}{\gamma_a C_{a0}} \right\} \left\{ 1 - \frac{C_2' \xi_2}{\phi(\xi_a - \xi_2)} \right\} \]

From eqn. 5.57,
\[ C_{1}' = 2 \left( \frac{\gamma_a}{\xi_1} \right) (\xi_a - \xi_2) \xi_2 C_{a0} \]
\[ \xi_a - \xi_2 = \frac{\gamma_1 C_{1}'}{2 \gamma_a \xi_2 C_{a0}} \]
\[ p-1 = \frac{1}{2} \left( \frac{C_{1}'}{(C_{10} - C_1')} \right) \left\{ \frac{\gamma_a C_{a0} + \gamma_2 (C_{20} - C_2')}{\gamma_a C_{a0}} \right\} \left\{ 1 - \frac{C_2' \xi_2}{\phi(\xi_a - \xi_2)} \right\} \]

Substituting the value of \( \phi \) and simplifying,
\[ p-1 = \frac{1}{2} \left( \frac{C_{1}'}{(C_{10} - C_1')} \right) \left\{ \frac{\gamma_a C_{a0} + \gamma_2 (C_{20} - C_2')}{\gamma_a C_{a0}} \right\} \left\{ 1 - \frac{\gamma_a C_{a0} C_2'}{(C_{20} - C_2') \gamma_1 C_1' \xi_2} \right\} \]

.. 5.75
Eqn. 5.75 represents the spacing coefficient for different additive concentrations.

5.3. **Experimental verification:**

5.3.1. **Experimental:**

The agar agar gel of desired inner electrolyte concentration was prepared as discussed in the Chapter III. 1% (by weight) agar agar gel was used to study the effect of additives. The preliminary observations showed that well defined rings were obtained when the concentration of the inner electrolyte (magnesium sulphate) was 0.081 mole/dm$^3$ and that of the outer electrolyte (aqueous ammonia) was 14.67 mole/dm$^3$. Hence such an optimum condition was used to study the influence of the additives on the velocity constant, spacing coefficient and the flocculation value.

Potassium, cadmium, cobalt, copper and aluminium sulphates were taken as additives. They were taken along with the inner electrolyte in the gel. The concentrations of the additives ($C_{a0}$) were varied from 0.3 to 6.5 milli mole/dm$^3$. The phenolphthalein indicator was also taken along with the gel to indicate the position of the diffusion front clearly. The positions of the rings and the diffusion fronts were measured using cathetometer. The experiments were repeated thrice and in each trial consistent values were obtained.
5.3.2. **Result:**

The dependence of the velocity constant on the concentration of additive is represented in Fig. 5.1. From figure it is found that the velocity constant decreases with the increase in the concentration of the additive. They represent the conditions when potassium, cadmium, cobalt, copper and aluminium sulphates were taken as the additive. Fig. 5.2 represents the variation of the spacing coefficient with the concentration of additive, during the periodic crystallisation of magnesium hydroxide.

The flocculation values were calculated as explained in the section 3.4.7. Fig. 5.3 represents the flocculation values for different concentrations of the additives, the additives being potassium, cadmium, cobalt, copper and aluminium sulphates.

5.3.3. **Discussion:**

The additives slow down the diffusion velocity with the increase in their concentrations as shown in Fig. 5.1. The effect is found to be very small in the case of the monovalent additive potassium sulphate and very large in the case of the trivalent additive aluminium sulphate. This can be explained qualitatively as follows. In hydrogels like agar agar, a network structure is formed with the
Fig. 5.1 The dependence of the velocity constant on the concentration of the additive.

1) K₂SO₄  2) CdSO₄  3) CoSO₄  4) CuSO₄  5) Al₂(SO₄)₃
water, bound to the fibrous particles of the polysaccharide. The interspaces between the fibrous particles act as capillaries for the diffusion. As a result of the reaction between the diffusing electrolyte and the one impregnated in the gel, a colloidal solution of magnesium hydroxide is formed. Flocculation occurs only due to the neutralisation of the charges of the colloidal sol by the ions of opposite charge in the excess of diffusing electrolyte. The diffusion front precedes the flocculation front.

The diffusion velocity depends on the viscosity of the colloidal sol. According to Einstein (35), the viscosity of the colloidal sol has a linear relationship to the viscosity of the liquid containing the colloidal particles and the concentration of the colloidal sol. The concentration denotes the number of ions in the solution. Thus it is clear that the presence of additives increases the ionic concentration of the colloidal solution, thereby increasing the viscosity. The increase of viscosity thereby reduces the diffusion velocity. The number of ions of colloidal solutions of same molarity has a linear relationship to the valency of the additive. Hence trivalent additive increases the viscosity to a greater extent than divalent or monovalent one. This leads to the larger decrease in the velocity constant by a trivalent additive. Further the additive potassium sulphate
leads to the formation of a soluble reaction product, whereas the other additives give insoluble products. This explains the very small effect of potassium sulphate and relatively large effect of other additives.

A quantitative explanation of the observed influence of the additives on the velocity constant can be given using eqn. 5.62. For computing the velocity constant, the following experimental data were employed.

\[ C_{10} = 14.68 \text{ mole/dm}^3 \]
\[ C_{20} = 0.081 \text{ mole/dm}^3 \]
\[ Y_1 = 1 \]
\[ Y_2 = 2 \]
\[ D_1 = 2.8775 \times 10^{-5} \text{ cm}^2/\text{sec}. \]

\[ D_1 \], the coefficient of diffusion of the diffusing outer electrolyte at infinite dilution was evaluated using the following Nernst equation (36).

\[ D_1 = 8.931 \times 10^{-10} \text{ T} \frac{(\lambda_+)(\lambda_\text{e})}{(\lambda_+)+(\lambda_-)} \frac{(Z_+)+(Z_-)}{Z_+Z_-} \approx 5.76 \]

where \( \lambda_+ \) and \( \lambda_- \) are the ionic conductivities of the positive and negative ions at infinite dilution and \( Z_+ \) and \( Z_- \) are the valencies of the respective ions.
The experimental values of $C_{q0}$ ranging from 0.3 to 6.5 milli mole/dm$^3$ were also used for the computation. Moreover computations were carried out for additives of different valencies, potassium sulphate ($\gamma_a = 1$), cadmium sulphate ($\gamma_a = 2$) and aluminium sulphate ($\gamma_a = 3$). Different values of $C_{1}'$ and $C_{2}'$ were chosen for the computation. It was observed that $C_{1}'$ and $C_{2}'$ had great influence on the velocity constant. Further it was found that the calculated value closely agreed with the experimental values at some specific values of $C_{1}'$ and $C_{2}'$. Such values of $C_{1}'$ and $C_{2}'$ which yield comparable value of the velocity constant of magnesium hydroxide system, varies with the concentration of the monovalent, divalent and trivalent additives as expected from eqns. 5.57 and 5.60.

Table 5.1 represents the computed values of $K$ for different types of additives with various concentrations. Aqueous ammonia is a very weak base and so its degree of dissociation is very small (37). So the concentration of $\text{OH}^-$ ions in the outer electrolyte is not the same as that of the outer electrolyte. Hence in computing $K$ the degree of ionisation of the outer electrolyte as well as that of the inner electrolyte (38) were taken into consideration.

In the experimental determination of the velocity constant for the periodic crystallisation of magnesium
### Table 5.1

Computed and experimental values of $K$ for different concentrations of the additives.

<table>
<thead>
<tr>
<th>$\gamma_a$</th>
<th>$C_{\text{a0}}$ (m mole/dm$^3$)</th>
<th>$K_{\text{PP}} \times 10^2$</th>
<th>$K_{\text{PI}} \times 10^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.1476</td>
<td>0.8583</td>
<td>2.6110</td>
</tr>
<tr>
<td></td>
<td>3.4428</td>
<td>0.8203</td>
<td>2.6060</td>
</tr>
<tr>
<td></td>
<td>5.7380</td>
<td>0.7831</td>
<td>2.5790</td>
</tr>
<tr>
<td></td>
<td>8.0332</td>
<td>0.7601</td>
<td>2.5770</td>
</tr>
<tr>
<td></td>
<td>0.7115</td>
<td>0.8560</td>
<td>2.3850</td>
</tr>
<tr>
<td></td>
<td>1.4230</td>
<td>0.8350</td>
<td>2.2600</td>
</tr>
<tr>
<td></td>
<td>2.1345</td>
<td>0.8167</td>
<td>2.2120</td>
</tr>
<tr>
<td></td>
<td>2.8460</td>
<td>0.7991</td>
<td>2.0860</td>
</tr>
<tr>
<td></td>
<td>3.5575</td>
<td>0.7825</td>
<td>2.0600</td>
</tr>
<tr>
<td></td>
<td>4.9805</td>
<td>0.7522</td>
<td>2.0000</td>
</tr>
<tr>
<td></td>
<td>6.4035</td>
<td>0.7265</td>
<td>1.9770</td>
</tr>
<tr>
<td></td>
<td>7.1150</td>
<td>0.7143</td>
<td>1.9270</td>
</tr>
<tr>
<td></td>
<td>7.8265</td>
<td>0.7036</td>
<td>1.9000</td>
</tr>
<tr>
<td></td>
<td>8.5380</td>
<td>0.6941</td>
<td>1.8980</td>
</tr>
<tr>
<td>2</td>
<td>0.3176</td>
<td>0.8644</td>
<td>2.1340</td>
</tr>
<tr>
<td></td>
<td>0.6346</td>
<td>0.8498</td>
<td>2.0750</td>
</tr>
<tr>
<td></td>
<td>0.9519</td>
<td>0.8364</td>
<td>1.9750</td>
</tr>
<tr>
<td></td>
<td>1.2692</td>
<td>0.8240</td>
<td>1.9450</td>
</tr>
<tr>
<td></td>
<td>1.5865</td>
<td>0.8129</td>
<td>1.9180</td>
</tr>
<tr>
<td></td>
<td>1.9038</td>
<td>0.8032</td>
<td>1.9040</td>
</tr>
<tr>
<td></td>
<td>2.2211</td>
<td>0.7930</td>
<td>1.8700</td>
</tr>
<tr>
<td></td>
<td>2.5384</td>
<td>0.7838</td>
<td>1.8490</td>
</tr>
<tr>
<td></td>
<td>2.8557</td>
<td>0.7744</td>
<td>1.8040</td>
</tr>
</tbody>
</table>
hydroxide, phenolphthalein was taken as the indicator along with the inner electrolyte in the agar agar gel. Such a method was followed for the periodic crystallisation of magnesium hydroxide in the presence of additives also. Due to the diffusion of the OH- ions into the gel, the pH of the gel solution increased to a value greater than 8.3. The location where the pH of the gel solution was greater than 8.3, was indicated by a front of a distinct colour change from white to pink. This colour front or pH front travelled continuously along the gel. In the experiment the velocity constant of this pH front is determined. So the experimental value of the velocity constant is that of pH front ($K_{ph}$).

In the theoretical consideration, eqn. 5.62 represents the velocity constant of the precipitation front ($K_{PF}$) where the ionic product exceeds the critical value. Thus the computed value of $K$ gives $K_{PF}$.

Moreover in the experiment, it was observed that at any location, the precipitation front passed a certain time interval after the passage of the pH front. Thus at any time the precipitation front lagged behind the pH front by a certain distance. Kai et al (39) have also reported such an observation. This shows that $K_{PH} > K_{PF}$. In Table 5.2 also it is observed that $K_{PH} > K_{PF}$. 
If \( x_{\text{PP}} \) and \( x_{\text{pH}} \) are the positions of the precipitation front and pH front from the gel boundary after \( t \) seconds from the start of the experiment,

\[
x_{\text{pH}} - x_{\text{PP}} = (K_{\text{pH}} - K_{\text{PP}}) t^{1/2}
\]

The distance by which the precipitation front lags the pH front at any instant of time, can be calculated from eqn. 5.77. The calculated values are found to be within the experimentally observed range.

The influence of the additives on the spacing coefficient is diagrammatically represented in Fig. 5.2. The spacing coefficient decreases with the increase in the concentration of an added electrolyte. Moreover, comparison of the effect of added electrolyte of similar molar concentration shows that the reduction in the spacing coefficient increases with the increase in the valency of the added cations. A qualitative explanation of this effect can be given based on the decrease in the solubility of the precipitate due to the added electrolyte.

According to Wagner, the spacing coefficient is smaller if the solubility of the precipitate formed is smaller. Thus the increase in the concentration of the added electrolyte should decrease the solubility of the precipitate.
Fig. 5.2 The variation of spacing coefficient with the concentration of the additive.

1) K$_2$SO$_4$ 2) CdSO$_4$ 3) CoSO$_4$ 4) Al$_2$(SO$_4$)$_3$ 5) CuSO$_4$
The diffusing anion reacts simultaneously with the inner reactant and the additive. The latter two have a common anion as a result of which two sparingly soluble salts with common anion are formed. The solubility of the sparingly soluble salt produced by the inner reactant is thus lowered by that formed due to the added electrolyte (40). A quantitative expression for the solubility of the sparingly soluble salt after the addition of another sparingly soluble salt can be found.

Let $S_o$ be the solubility of the sparingly soluble salt $P_{2} \gamma_{2} \gamma_{1}$ formed due to the reaction of the outer electrolyte and the inner electrolyte. By the solubility product principle,

$$\left(\gamma_{2} S_{0}\right)^{\frac{1}{2}} \left(\gamma_{1} S_{0}\right)^{\frac{1}{2}} = K_S$$ .. 5.78

Another sparingly soluble salt $P_{1} \gamma_{1}$ is formed due to the reaction of the outer electrolyte and the additive. Let $C_a$ be the concentration of this salt formed. This adds $\gamma_{a} \beta C_a$ anions to the solution, thus changing the solubility of the original salt to $S_o$. $\beta$ is the ionic degree of dissociation having value less than 1. Again by the solubility product principle,

$$\left[\gamma_{1} S\right]^\frac{1}{2} \left[\gamma_{2} S + \gamma_{a} \beta C_a\right]^\frac{1}{2} = K_S$$ .. 5.79
Eqns. 5.78 and 5.79 give,

\[ S \gamma_1 [\gamma_2 S + \gamma_a \beta C_a] \gamma_2 = S_0 \gamma_2 \gamma_2 S_0 \gamma_2 \] .. 5.80

considering the simple case of \( \gamma_1 = \gamma_2 = 1 \) and using the binomial approximation, one gets

\[ S = \frac{S_0^2}{\beta \gamma_a C_a} \] .. 5.81

Thus the salts with common ion decrease the solubility to nearly the same extent and are in approximate agreement with the values computed on the basis of the simple solubility product principle (41). The decrease in the solubility by the additives of same molar concentration depends on the valency of the cations. Further decrease in solubility leads to the decrease in the spacing coefficient. Thus the curves in Fig. 5.2 are qualitatively explained.

A quantitative explanation of the effect of additives on spacing coefficient can be given using eqn. 5.75. For computing the spacing coefficient, the experimental values of \( C_{10}, C_{20}, C_{a0}, \gamma_1, \gamma_2 \) and \( \gamma_a \) were used. Table 5.2 represents the computed and experimental values of \( (p-1) \) for different types of additives with various concentrations. While computing \( (p-1) \) also, the degrees of ionisation of the outer and inner electrolytes were taken into consideration.
Table 5.2
The theoretical and experimental values of spacing coefficient for different concentrations of the additives.

<table>
<thead>
<tr>
<th>( \gamma_a )</th>
<th>( C_{a0} ) mol/dm(^3)</th>
<th>Spacing coefficient ( \gamma )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>theoretical</td>
<td>experimental</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1476</td>
<td>1.4389</td>
<td>1.4390</td>
</tr>
<tr>
<td>3.4428</td>
<td>1.4322</td>
<td>1.4320</td>
</tr>
<tr>
<td>5.7380</td>
<td>1.4292</td>
<td>1.4290</td>
</tr>
<tr>
<td>8.0332</td>
<td>1.4182</td>
<td>1.4180</td>
</tr>
<tr>
<td>0.7115</td>
<td>1.3449</td>
<td>1.3450</td>
</tr>
<tr>
<td>1.4230</td>
<td>1.3311</td>
<td>1.3310</td>
</tr>
<tr>
<td>2.1345</td>
<td>1.3122</td>
<td>1.3120</td>
</tr>
<tr>
<td>2.8460</td>
<td>1.3072</td>
<td>1.3070</td>
</tr>
<tr>
<td>3.5575</td>
<td>1.3042</td>
<td>1.3040</td>
</tr>
<tr>
<td>4.9805</td>
<td>1.3022</td>
<td>1.3020</td>
</tr>
<tr>
<td>6.4035</td>
<td>1.2921</td>
<td>1.2920</td>
</tr>
<tr>
<td>7.1150</td>
<td>1.2902</td>
<td>1.2900</td>
</tr>
<tr>
<td>7.8265</td>
<td>1.2832</td>
<td>1.2830</td>
</tr>
<tr>
<td>8.5380</td>
<td>1.2732</td>
<td>1.2730</td>
</tr>
<tr>
<td>0.3176</td>
<td>1.3116</td>
<td>1.3120</td>
</tr>
<tr>
<td>0.6346</td>
<td>1.3061</td>
<td>1.3060</td>
</tr>
<tr>
<td>0.9519</td>
<td>1.3011</td>
<td>1.3010</td>
</tr>
<tr>
<td>1.2692</td>
<td>1.2931</td>
<td>1.2930</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.5865</td>
<td>1.2771</td>
<td>1.2770</td>
</tr>
<tr>
<td>1.9038</td>
<td>1.2571</td>
<td>1.2570</td>
</tr>
<tr>
<td>2.2211</td>
<td>1.2501</td>
<td>1.2500</td>
</tr>
<tr>
<td>2.5384</td>
<td>1.2401</td>
<td>1.2400</td>
</tr>
<tr>
<td>2.8557</td>
<td>1.3261</td>
<td>1.3260</td>
</tr>
</tbody>
</table>
It is observed that the experimental values of the spacing coefficient for magnesium hydroxide system closely agree with the theoretical values for different types of additives of various concentrations.

In eqns. 5.62 and 5.75, $C_1'$ and $C_2'$ represent the concentration of the ions $P$ and $Q$ very close to the precipitation front, contributed by the outer and inner electrolytes. It is found that the value of $C_1'$ and $C_2'$ have great influence on the values of $K$ and $P$. The values of $C_1'$ and $C_2'$ which yield comparable values of the velocity constant and spacing coefficient, vary with the concentration of the monovalent, divalent and trivalent additives. Moreover they ($C_1'$ and $C_2'$) are found to be very low as assumed in the theoretical consideration. (Table 5.3).

In Fig. 5.3 it is found that the flocculation value decreases with the concentration of the additive. A qualitative explanation for this effect can be given as follows. In the system investigated negatively charged magnesium hydroxide sol is formed at first. In the additive free system, the excess of diffusing electrolyte is the contributor of the cations for the flocculation. But the free cations of the additives in the gel also participate in the
Table 5.3

The values of $C_1'$ and $C_2'$ which give comparable values for velocity constant and spacing coefficient corresponding to different concentrations of the additives.

<table>
<thead>
<tr>
<th>$\gamma_a$</th>
<th>$C_{a0}$ (mole/dm$^3$)</th>
<th>$C_1' \times 10^2$ (mole/dm$^3$)</th>
<th>$C_2' \times 10^2$ (mole/dm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.1476</td>
<td>0.1290</td>
<td>1.0819</td>
</tr>
<tr>
<td></td>
<td>3.4428</td>
<td>0.3484</td>
<td>0.1483</td>
</tr>
<tr>
<td></td>
<td>5.7380</td>
<td>0.5317</td>
<td>0.0637</td>
</tr>
<tr>
<td></td>
<td>8.0332</td>
<td>0.6745</td>
<td>0.0395</td>
</tr>
<tr>
<td></td>
<td>0.7115</td>
<td>0.1250</td>
<td>1.1517</td>
</tr>
<tr>
<td></td>
<td>1.4230</td>
<td>0.2284</td>
<td>0.3451</td>
</tr>
<tr>
<td></td>
<td>2.1345</td>
<td>0.3089</td>
<td>0.1887</td>
</tr>
<tr>
<td></td>
<td>2.8460</td>
<td>0.3880</td>
<td>0.1196</td>
</tr>
<tr>
<td>2</td>
<td>3.5575</td>
<td>0.4606</td>
<td>0.0848</td>
</tr>
<tr>
<td></td>
<td>4.9805</td>
<td>0.5919</td>
<td>0.0514</td>
</tr>
<tr>
<td></td>
<td>6.4035</td>
<td>0.6863</td>
<td>0.0382</td>
</tr>
<tr>
<td></td>
<td>7.1150</td>
<td>0.7322</td>
<td>0.0336</td>
</tr>
<tr>
<td></td>
<td>7.8265</td>
<td>0.7626</td>
<td>0.0309</td>
</tr>
<tr>
<td></td>
<td>8.5380</td>
<td>0.7809</td>
<td>0.0295</td>
</tr>
<tr>
<td>3</td>
<td>0.3176</td>
<td>0.0771</td>
<td>3.0252</td>
</tr>
<tr>
<td></td>
<td>0.6346</td>
<td>0.1462</td>
<td>0.8416</td>
</tr>
<tr>
<td></td>
<td>0.9519</td>
<td>0.2091</td>
<td>0.4113</td>
</tr>
<tr>
<td></td>
<td>1.2692</td>
<td>0.2634</td>
<td>0.2595</td>
</tr>
<tr>
<td></td>
<td>1.5865</td>
<td>0.3029</td>
<td>0.1691</td>
</tr>
<tr>
<td></td>
<td>1.9038</td>
<td>0.3292</td>
<td>0.1660</td>
</tr>
<tr>
<td></td>
<td>2.2211</td>
<td>0.3643</td>
<td>0.1356</td>
</tr>
<tr>
<td></td>
<td>2.5384</td>
<td>0.3904</td>
<td>0.1181</td>
</tr>
<tr>
<td></td>
<td>2.8557</td>
<td>0.4216</td>
<td>0.1013</td>
</tr>
</tbody>
</table>
Fig. 5.3 Flocculation value for different concentrations of the additives.

1) K$_2$SO$_4$  2) CdSO$_4$  3) CoSO$_4$  4) Al$_2$(SO$_4$)$_3$  5) CuSO$_4$
process of flocculation of the colloidal sol. Thus the concentration of the diffusing electrolyte required for neutralisation is decreased.

According to Schulze-Hardy rule, the valency of the cations plays a dominating role in the flocculation of the negative sol. This explains the decrease in the flocculation value for the various additives at the same molar concentrations. The deviation in the case of copper may be due to the formation of $[\text{Cu(NH}_3)_4]^{2+}$ ion. The flocculation value of ions of same valency depends on the ionic radius (42). This explains the difference in the flocculation value for Cd**, Co** and Cu** ions.

5.4. Conclusion:

Expressions have been derived for the velocity constant and the spacing coefficient incorporating the valency and the concentration of the additive for periodic crystallisation in gel. The influence of the additives on the periodic crystallisation of magnesium hydroxide in agar agar gel has been investigated experimentally. The theoretical expressions derived are compared with the experimental results. It is observed that a very close agreement exists between the theoretical and experimental results.
The effect of additives on the flocculation value is also investigated experimentally. A qualitative explanation is given for the observed result.
References