JOURNAL OF MATERIALS SCIENCE 28 (1993) 6357–6359

# Estimation of diffusion coefficients and a plausible identification of species from one-dimensional Liesegang-ring formations in multicomponent systems

G. VARGHESE
*Department of Physics, St. Berchmans' College, Changanacherry, Kerala, India*
M. A. ITTYACHEN, C. JOSEPH
*School of Pure and Applied Physics, Mahatma Gandhi University, Priyadarsini, Kottayam, Kerala, 686560, India*

Liesegang-ring phenomenon has been explained for two-component systems by many workers. In this paper an attempt has been made to extend the theory to three-component systems. It is observed that two types of rings are formed consisting of two types of species. The experimental observations verify the validity of the proposed theory. This theory can also be extended to multicomponent systems.

## 1. Introduction

R. E. Liesegang first reported [1] the formation of a periodic precipitation pattern while studying the reaction of silver nitrate on a gel impregnated with potassium chromate. The phenomenon has since been examined by a large number of investigators and many theories have been suggested [2–8] to explain the rhythmic structure. Several authors have also investigated the role of diffusion in the process of periodic crystallization. Using a simple mathematical model, Kirov [9] explained the diffusion-controlled growth in a qualitative way and calculated the diffusion coefficients of the ions in the gel medium. Matalon and Packter [10] have shown that the sol protection in the gel and diffusion are two important factors which control the rhythmic precipitation. Recently Henisch and Gracia-Ruiz [11, 12] have developed a computer-simulation technique to solve the diffusion-controlled problem as a time function.

## 2. Diffusion and rhythmic precipitation

Since the precipitation is controlled by a diffusion mechanism the theoretical framework involves the application of Fick's diffusion equations. According to the diffusion theory, put forward by Neumann and Costeanu [13] and by Carl Wagner [5], the diffusant, M, reaches the gel, containing, a precipitant, P, hence a molecule of the type MP is formed due to the following irreversible chemical reaction:

$$M^{\pm} + P^{\mp} \rightarrow MP \tag{1}$$

Precipitation occurs as a result of the coagulation of this dispersion. The precipitated materials, or crystallites, appear on a ring in the gel medium. As time advances, the diffusion proceeds further and the number of rings gradually increases. The rhythmicity of the pattern is due to some minor perturbations in the diffusion process. The stability of these metastable sols is important in the process of crystallization. To sustain the nucleus formation the concentration profiles of the M-type and P-type ions must satisfy the equation

$$C_M C_P = K$$

and (2)

$$\frac{\partial K}{\partial x} = 0$$

where $K$ is a constant.

The variation in the concentrations of the ions is described by Fick's law:

$$\frac{\partial C_M}{\partial t} = D\frac{\partial^2 C_M}{\partial x^2} \tag{3}$$

$$\frac{\partial C_P}{\partial t} = D\frac{\partial^2 C_P}{\partial x^2} \tag{4}$$

where $D$ is the diffusion coefficient, which is assumed to be the same for both ions at the nucleation site (at $x = x_1$). The distance, $x$, is measured from the gel–solution interface with the positive direction in the direction of the diffusion of the M-type ions (Fig. 1).

Upon writing the initial conditions for the concentrations as

$$C_M \approx C_{M0} \quad (x < 0, t = 0)$$

and

$$C_P \approx C_{P0} \quad (x > 0, t = 0)$$

0022-2461

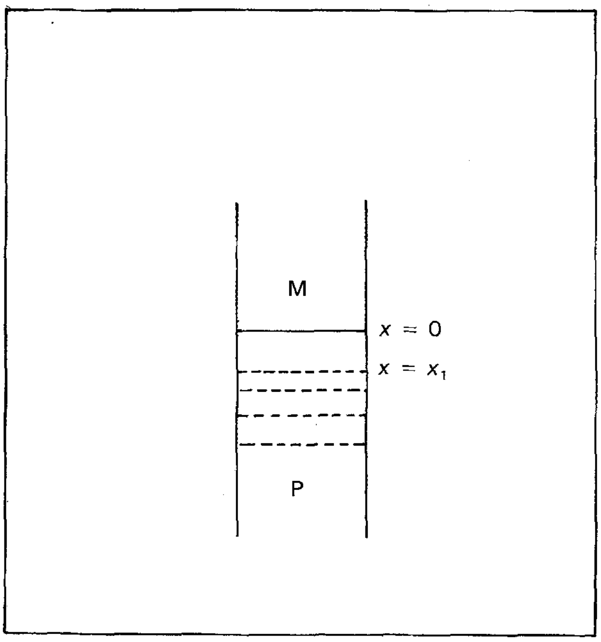

*Figure 1* The Liesegang-ring systems in two component-systems resulting from one-dimensional diffusion.

and restricting $C_{MO}$ to

$$C_{MO} \gg C_{PO}$$

Wagner obtained the following result

$$C_{PO} \simeq \frac{C_{MO}\exp[-x^2(1)]}{\alpha_1(t)\,\beta_1(t)} \tag{5}$$

where $\alpha_1(t)$ and $\beta_1(t)$ are functions of time. This is a general formula when two types of ions are interacting in the medium. The presence of one more diffusant, N, in the supernatant solution may produce three different kinds of molecules if the chemical conditions are favourable (MP, NP and MNP); and each species may generate their own precipitation zones, as expected from Equation 4. (Fig. 2). Hence two more relations for $C_{PO}$ can be obtained.

$$C_{PO} \simeq \frac{C_{NO}\exp[-x^2(2)]}{\alpha_2(t)\,\beta_2(t)} \tag{6}$$

$$C_{PO} \simeq \frac{(C_{MO} + C_{NO})\exp[-x^2(3)]}{\alpha_3(t)\,\beta_3(t)} \tag{7}$$

with $C_{NO}$ as the initial concentration of the N-type ions at $x < 0$ and at $t = 0$.

## 3. Experimental observations

During the process of crystallization of mixed rare-earth oxalates [14, 15] in sodium meta silicate gel two of the authors observed two kinds of ring systems with lanthanum and copper as cations. The experiment was carried out in glass tubes containing a vertical column of meta silicate gel, charged with oxalic acid. Measured volumes of lanthanum-nitrate and copper-nitrate solutions were poured over the gel as the source of the cations. After hours of diffusion, well-defined periodic ring structures were seen in the gel. When the diffusants meet oxalate ions in the gel they combine and form salts of lanthanum oxalate and lanthanum–copper oxalates. Lanthanum-oxalate crystals are transparent and prismatic while the other oxalates are bluish-green spherulites. The ring systems were examined carefully and their time of formation and distance from the gel–solution interface was measured. The crystal samples were identified by conventional techniques.

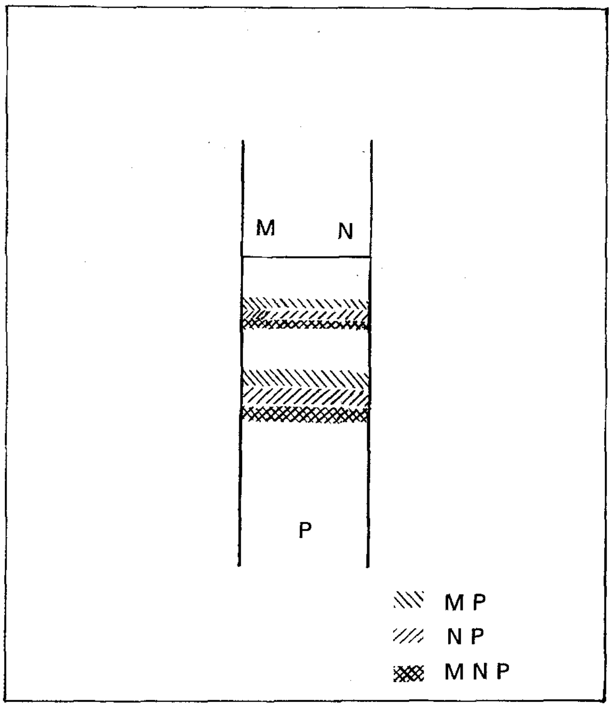

*Figure 2* Rhythmic ring-structure patterns of different species in multicomponent systems.

### 3.1. Verification of empirical relations

The ring systems were found to obey the empirical relations [16, 17]; see Table I. For each set of rings

$$\frac{x_{n+1}}{x_n} = \text{constant} \tag{8}$$

and

$$\frac{x_n}{(t_n)^{1/2}} = \text{constant} \tag{9}$$

Varying the initial concentrations of the upper reactants verified the linear relationship between the concentrations and $x$ in each set of rings (Fig 3).

### 3.2. Estimation of diffusion coefficients

To a good approximation, the diffusion coefficients can be estimated [18, 19] using the following formulae

$$D \simeq \frac{x^2/t}{4\ln(C_{NO}/C_{PO})} \tag{10}$$

$$D' \simeq \frac{x^2/t}{4\ln[(C_{MO} + C_{NO})/C_{PO}]} \tag{11}$$

In real experiments the inner electrolyte concentration is kept constant throughout. From the observed rate of movement of the advancing boundary, the $D$ values are estimated (see Table II).

TABLE I Verification of the empirical relations

(a) Outer electrolytes: 0.4 M copper nitrate and 0.5 M lanthanum nitrate

| Type of species | $n$ | $x$ (cm) | $t$ (h) | $x^2/t$ (m$^2$ h$^{-1}$) | $x_{n+1}/x_n$ |
|---|---|---|---|---|---|
| I | 1 | 0.751 | 6.5 | 0.086 | |
| | 2 | 0.856 | 8.5 | 0.086 | 1.140 |
| | 3 | 0.976 | 11 | 0.086 | 1.140 |
| II | 1 | 0.795 | 7 | 0.090 | |
| | 2 | 0.914 | 9.25 | 0.090 | 1.149 |
| | 3 | 1.048 | 12 | 0.091 | 1.146 |

(b) Outer electrolytes: 0.6 M copper nitrate and 0.5 M lanthanum nitrate

| Type of species | $n$ | $x$ (cm) | $t$ (h) | $x^2/t$ (m$^2$ h$^{-1}$) | $x_{n+1}/x_n$ |
|---|---|---|---|---|---|
| I | 1 | 1.12 | 10.75 | 0.116 | |
| | 2 | 1.197 | 12.5 | 0.114 | 1.070 |
| | 3 | 1.284 | 14.5 | 0.114 | 1.072 |
| II | 1 | 1.174 | 11 | 0.125 | |
| | 2 | 1.276 | 13 | 0.125 | 1.090 |
| | 3 | 1.391 | 15.5 | 0.125 | 1.090 |

(c) Outer electrolytes: 0.5 M copper nitrate and 0.2 M lanthanum nitrate

| Type of species | $n$ | $x$ (cm) | $t$ (h) | $x^2/t$ (m$^2$ h$^{-1}$) | $x_{n+1}/x_n$ |
|---|---|---|---|---|---|
| I | 1 | 0.851 | 10.5 | 0.0690 | |
| | 2 | 0.951 | 13 | 0·0695 | 1.118 |
| | 3 | 1.063 | 16.5 | 0.0684 | 1.117 |
| II | 1 | 0.905 | 11 | 0.075 | |
| | 2 | 1.025 | 14 | 0.075 | 1.133 |
| | 3 | 1.159 | 18 | 0.075 | 1.131 |

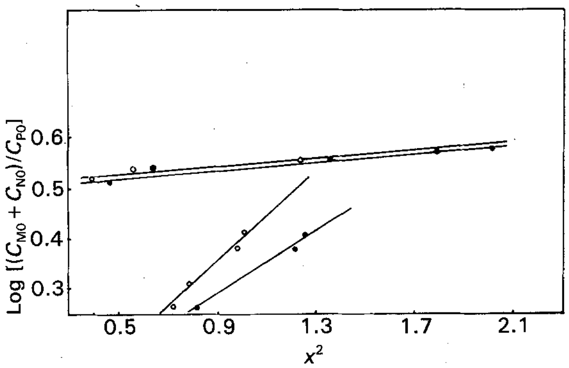

*Figure 3* The dependence of the concentration of the interacting ions on the ring distance: (○) type I, and (●) type II.

TABLE II Estimation of the diffusion coefficients (outer electrolytes, copper nitrate and lanthanum nitrate solutions (CN and LN); inner electrolyte, 0.5 M oxalic acid)

| Conc. of outer electrolytes (mol) | Type of species | $x^2/t$ (cm$^2$ s$^{-1}$) | $D$ ($\times 10^{-5}$) (cm$^2$ s$^{-1}$) |
|---|---|---|---|
| 0.6 CN, 0.5 LN | I | 0.115 | 1.493 |
| 0.6 CN, 0.5 LN | II | 0.125 | 0.672 |
| 0.8 CN, 0.5 LN | I | 0.133 | 1.173 |
| 0.8 CN, 0.5 LN | II | 0.144 | 0.754 |
| 0.4 CN, 0.5 LN | I | 0.087 | 3.482 |
| 0.4 CN, 0.5 LN | II | 0.090 | 0.502 |

## 4. Conclusion

The coagulation hypothesis based on the diffusion theory is generally found to be true in the case of two-component systems. If one more component is incorporated into the system, the diffusion theory can be extended to a three-component system; this was attempted here. The precipitation of either MP, NP or MNP can take place, depending on the diffusion coefficients and the chemical environment prevailing in the medium. The theory proposed here agrees in the case of two distinct types of crystallites which segregate in two different regions after following a periodic arrangement. The temporal and spatial laws were verified for each system. This technique can be used as a powerful method of species identification. As the temporal and spatial constants are different for different species, the formations of different crystallites can easily be suggested in a multicomponent system. This theory can be generalized in the case of multicomponent systems.

## References

1. R. E. LIESEGANG, *Z. Physik* **23** (1897) 365.
2. W. OSTWALD, *Z. Physik. Chem.* **27** (1897) 265.
3. N. R. DHAR and A. C. CHATERJEE, *Kolloid. Z* **31** (1922) 15.
4. S. C. BRADFORD, *ibid.* **30** (1922) 364.
5. C. WAGNER, *J. Colloid Sci.* **5** (1950) 85.
6. A. VANHOOK, *J. Phys Colloid Chem.* **42** (1938) 1191.
7. SINOHARA, *J. Phys. Soc. Jpn.* **29** (1970) 1073.
8. K. M. PILLAI, V. K. VAIDYAN and M.A. ITTYACHEN, *Colloid Poly. Sci.* **258** (1980) 831.
9. G. K. KIROV, *J. Cryst. Growth* **15** (1972) 102.
10. R. MATALON and A. PACKTER, *J. Colloid Sci.* **10** (1950) 46.
11. H. K. HENISCH and J. M. GRACIA-RUIZ, *J. Cryst. Growth,* **75** (1986) 195.
12. *Idem., ibid.* **75** (1986) 203.
13. K. NEUMANN and V. COSTEANU, *Kolloid. Z.* **84** (1940) 130.
14. G. VARGHESE and M. A. ITTYACHEN, *Cry. Res. Technol.* in (press).
15. *Idem. J. Mater. Sci. Lett.* **11** (1992) 916.
16. K. JABLCZYNSKI, *Bull. Soc. Chim,* France **4** (33) (1903) 1592.
17. H. W. MORCE and G. W. PIERCE, *Physik. Chem.* **45** (1903) 589.
18. K. V. KURIEN, V. K. VAIDYAN and M. A. ITTYACHEN, *Indian J. Pure Appl. Phys.* **21** (1983) 261.
19. S. M. DHARMA PRAKASH and P. MOHAN RAO, *J. Mater. Sci. Lett.* **8** (1989) 141.

*Received 25 November 1992*
*and accepted 1 June 1993*