Journal of Molecular Liquids 180 (2013) 70–73

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Studies on Liesegang rings of copper molybdate in agar gel medium

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ARTICLE INFO

Article history:
Received 6 September 2012
Received in revised form 10 December 2012
Accepted 3 January 2013
Available online 17 January 2013

Keywords:
Periodic precipitation
Liesegang rings
Copper molybdate
Time law
Spacing law
Width law

ABSTRACT

The present work deals with the studies on Liesegang ring formation of copper molybdate ions using copper sulphate as an outer electrolyte and sodium molybdate as an inner electrolyte. For this purpose 1% agar gel was used and the inner electrolyte concentration was chosen to be 0.025 M and 0.05 M. While outer electrolyte concentration was kept 0.5 M and 0.25 M. Morphological characteristics of Liesegang rings such as size of the ring, number of rings per day, and spacing between rings were studied. The concentration of reacting ions in the ring was estimated by atomic absorption spectrophotometer. The obtained results are quantitatively explained on the basis of spacing law, time law and width law. All basic laws were obeyed successfully by the system. It was observed that, the morphological characteristics of the rings were affected by the concentrations of inner and outer electrolytes.

1. Introduction

The periodic precipitation pattern is formed under the specific physicochemical conditions by diffusing an electrolyte (inner electrolyte) into the other electrolyte (outer electrolyte) present in the gel. The insoluble product precipitates rhythmically in band perpendicular to the direction of diffusion called Liesegang phenomenon. The presence of gel helps to study this phenomenon. It provides sedimentation of the precipitate and hydrodynamic turbulence [1]. The initial concentration of outer electrolyte is kept more than that of the inner electrolyte to increase diffusion flux [2]. The present paper reports the results on Liesegang rings formation of copper molybdate.

2. Experimental

Chemicals used for the experiments are AR grade, bacteriological agar gel powder (HiMEDIA, Laboratories, Mumbai), sodium molybdate (MERCK India), copper sulphate (Qualigen Chemicals). We have used a glass tube of 30 cm length with 0.8 cm inner diameter for studying the periodic precipitation. To measure the size and distance between the rings travelling microscope have been used. Desired concentration of sodium molybdate (inner electrolyte) solution containing 1% agar gel was prepared by heating it slowly to get clear gel. This was then poured into glass tubes until it became half full. The desired concentration of 15 ml copper sulphate (outer electrolyte) was then poured on the solidified gel and allowed to diffuse. To minimize the evaporation the tube was properly sealed. The system was kept at 25 °C in thermostat. The number of rings formed per day was noted for 2 weeks. After complete diffusion the size of the ring and spacing between two rings were measured by travelling microscope. The gel was removed from the tube; the rings were dissolved in slightly acidic water and diluted to 100 ml. The concentration of ions was estimated by using Atomic absorption spectrophotometer (LABINDIA - 7000). The Liesegang rings were studied for different concentrations of inner and outer electrolytes. The developed Liesegang rings of copper molybdate system are shown in Fig. 1.

3. Result and discussion

In the present work Cu^{2+} ions (A) diffuse in the gel containing MoO_4^- ions (B). As diffusion proceeds further in the gel, the chemical reaction between Cu^{2+} and MoO_4^- ions takes place as follows,

$$CuSO_4 + Na_2MoO_4 \rightarrow CuMoO_4 + Na_2SO_4.$$

The concentration of outer and inner electrolytes shows the influence on periodicity of Liesegang ring formation, width of the ring, time of ring appearance, and number of rings. In all cases the morphological characteristics of the system such as time required to form the ring '$\mathbf{t_n}$', distance of the ring from the interface of the gel '$\mathbf{X_n}$', width of rings '$\Delta\mathbf{X}$', and spacing between the rings '$\boldsymbol{\xi_n}$' were measured. The different empirical laws were also verified. The different parameters: time of formation, width, total number of rings, and spacing between the rings are recorded in Tables 1 and 2.

In general the Liesegang ring phenomenon should follow three basic laws; time law, spacing law, and width law [3].

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http://dx.doi.org/10.1016/j.molliq.2013.01.002

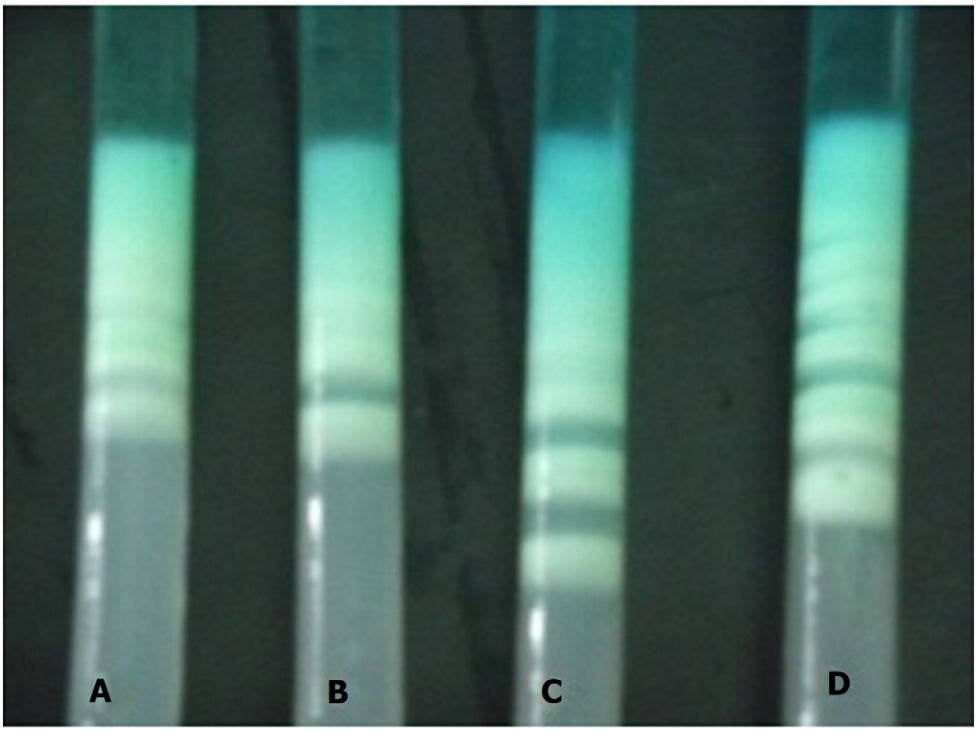

Fig. 1. Copper molybdate rings in 1% agar gel formed by copper sulphate (Conc. for tube A, C: 0.025 M and B, D: 0.05) and sodium molybdate (Conc. for tube A, B: 0.25 M and C, D: 0.5 M).

3.1. Verification of different laws of Liesegang rings

3.1.1. Verification of time law

The position of the band and its time of formation are interestingly related by a simple equation often called 'time law'. Morse and Piers [4] have framed a relation connecting the distance of the ring from the interface '$\mathbf{x_n}$' and the time of formation '$\mathbf{t_n}$' is known as the '*time law*'.

$$\mathbf{x_n}/\sqrt{\mathbf{t_n}} = \mathbf{a}\ \text{constant},$$
$$\mathbf{x_n}^2 \alpha\, \mathbf{t_n}.$$

The plot of $\mathbf{x_n}^2$ against $\mathbf{t_n}$ shows the time dependence of system (Fig. 2). The time required for the appearance of first ring was same in all the systems i.e. 48 h. When inner electrolyte concentration is 0.025 M time required for the appearance of the rings is more and numbers of the rings are less. The time law has been successfully obeyed by the copper molybdate system. When outer electrolyte concentration is 0.25 M it is observed that the numbers of the rings are less.

Table 1
Morphological parameters for Liesegang rings of copper molybdate in 1% agar gel having outer electrolyte: 0.5 M $CuSO_4$.

Conc. of inner electrolyte	No. of ring	$\Delta\mathbf{x}$ (cm)	$\mathbf{x_n}$ (cm)	$\mathbf{t_n}$ (h)	$\mathbf{x_n}^2/\mathbf{t_n}$ $_{cm}^2$ h^{-1}	$\mathbf{x_n}/\Delta\mathbf{x}$	Spacing coefficient 'a'	ξ_n (cm)
0.025 M	1	1.11	1.5	48	0.04	1.35	1.33	0.59
	2	0.35	2.0	72	0.05	5.7	1.60	0.75
	3	0.50	3.2	192	0.05	5.7	1.25	0.69
	4	0.70	4.0	216	0.07	5.8	1.3	1.00
	5	0.90	5.2	312	0.07	5.7		
0.05 M	1	1.11	1.1	48	0.04	0.9	1.63	1.00
	2	0.40	1.8	72	0.04	4.5	1.16	0.44
	3	0.59	2.1	96	0.04	3.5	1.23	0.65
	4	0.45	2.6	124	0.04	5.7	1.44	1.00
	5	0.65	3.1	240	0.04	4.1	1.22	1.15
	6	0.69	3.8	288	0.05	5.4		

3.1.2. Verification of width law

Width of the ring '$\Delta\mathbf{x}$' should be increased with their position '$\mathbf{x_n}$' according to the width law [1]. The variation of the width of the ring with diffusion depth is shown in Fig. 3.

The width of the ring generally increases with the distance of the ring from the gel interface. In the present case the size of the ring increases with the position of the ring from the second ring onwards. The solubility of the medium decreases due to ageing. So the critical concentration required for precipitation decreases and hence the width of the band increases with the age of gel [7].

3.1.3. Verification of spacing law

Jablczynsky [5,6] has formulated another relation connecting distance of consecutive rings $\mathbf{x_{n+1}}/\mathbf{x_n} = \mathbf{a}$ constant where, $a = 1 + p$. The relation is called spacing law and the quantity $(1 + p)$ is referred to as the spacing coefficient. The spacing coefficient 'p' is having characteristic values for particular system. The ratio of two successive bands measured from the surface of the gel tends to attain a value that is usually larger than 1. Jablczynsky derived this relation on the basis of thermidynamical argument and is supported by many experimental reports [8]. For various concentrations of inner and outer electrolyte concentrations spacing coefficient '**a**' obtained was >1 and is listed in Tables 1–2. It was

Table 2
Morphological parameters for Liesegang rings of copper molybdate in 1% agar gel having outer electrolyte: 0.25 M $CuSO_4$.

Conc. of inner electrolyte	No. of ring	$\Delta\mathbf{x}$ (cm)	$\mathbf{x_n}$ (cm)	$\mathbf{t_n}$ (h)	$\mathbf{x_n}^2/\mathbf{t_n}$ $_{cm}^2 h^{-1}$	$\mathbf{x}/\Delta\mathbf{x}$	Spacing coefficient 'a'	ξ_n (cm)
0.025 M	1	1.04	1.5	48	0.04	1.42	1.6	1.15
	2	0.42	2.4	96	0.04	5.64	1.33	0.94
	3	0.59	3.2	168	0.06	5.35	1.28	1.69
	4	0.80	4.1	216	0.07	5.12		
0.05 M	1	1.20	1.4	48	0.04	1.16	1.78	0.85
	2	0.70	2.5	144	0.04	3.55	1.44	1.60
	3	0.80	3.6	192	0.06	4.86		