

Role of salt effect and adsorption on the Liesegang ring formation of lanthanum molybdate

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Abstract. The effect of solubility of sparingly soluble lanthanum molybdate in the formation of Liesegang rings has been studied. The rings become distinct and clear with increasing acidity of the medium due to the salt effect. The concentration of the interacting solution for well-defined rings in silica gel medium has been obtained. The role of adsorption in the formation of clear spaces between consecutive rings is also discussed.

Keywords. Salt effect; adsorption; Liesegang ring formation; lanthanum molybdate.

1. Introduction

Periodic precipitation of a number of insoluble substances, better known as Liesegang rings were studied by a number of workers notably Dhar and Chatterji (1922, 1925), Bradford (1920), Shinohara (1971), Pillai *et al* (1980), Gnanam *et al* (1980), Kurien *et al* (1982) etc. The phenomenon has already been observed in many systems (Veil 1949) under varying condition (Isemura 1939; Bradford 1916) in aqueous (Morse 1930) and other non-gelatinous media (Spotz and Hirschfelder 1951). Various empirical relations (1903, 1926, 1980) have been developed to explain periodic formations in various systems. The present authors have investigated Liesegang ring formation in the barium and lanthanum molybdate systems (Kurien *et al* 1982) making use of empirical relations. The latter system is more precipitous and the solubility of its precipitate plays a significant role in the formation of rings. Like any other system, here also the rings are more closely packed at the contact of the interacting solution.

This paper describes the salt effect on the solubility of lanthanum molybdate in the formation of Liesegang rings. It also deals with the colloidal behaviour of lanthanum molybdate and the role of adsorption in producing periodic precipitation.

2. Experimental

A standard solution (1 S) of ammonium molybdate was prepared using am-

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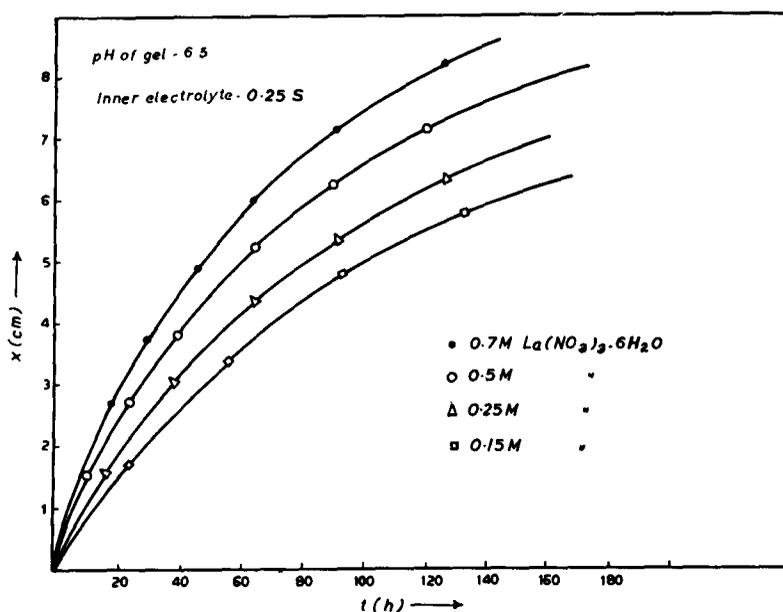


Figure 1. Plot showing the rate of precipitation front.

monium nitrate, concentrated nitric acid and ammonium molybdate. It was prepared by dissolving 2 g of ammonium molybdate and 2 g of ammonium nitrate in distilled water. To this solution concentrated nitric acid (6 ml) was gradually added and the whole system was cooled. The solution was then di-

Table 1. Nature of rings obtained for different chemical combinations.

pH	Outer electrolyte (M)	Inner electrolyte (M)	Number of rings (± 1)	Nature of the system
6.3 ± 0.2	0.5	0.005	12	Rings thickly crowded at the beginning
	0.3		11	Rings with distinguishable separation
	0.2		10	Rings with distinguishable separation
	1.0	0.01	19	Overcrowded rings with slight milky void spaces
	0.8		18	Good system of rings with well-defined sharp boundaries
	0.5		16	
6.8 ± 0.2	0.3	0.01	15	
	0.5		12	Rings with distinguishable separation but with slight milky void spaces
	0.4		11	
	0.3	0.02	9	Less distinct rings with milky void spaces
	0.5		10	
	0.4		9	
	0.3		7	

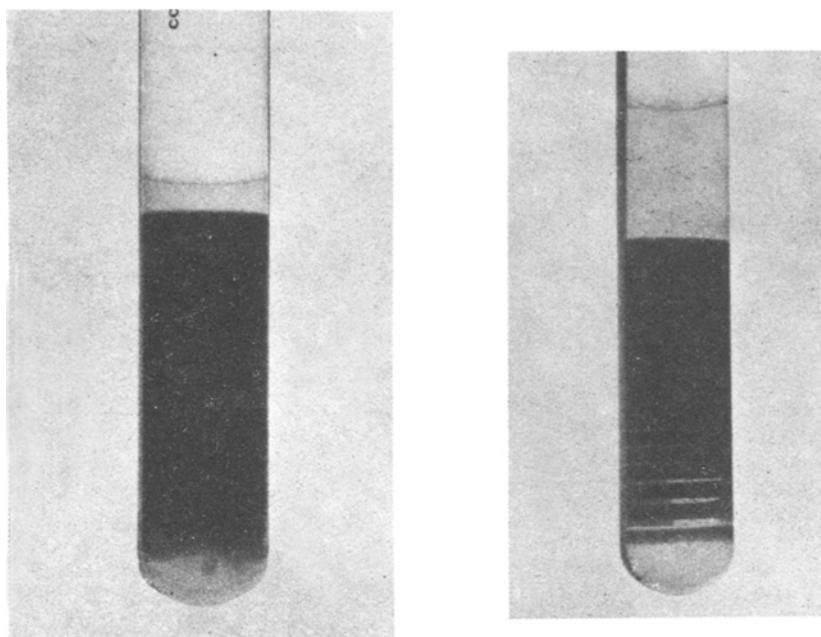
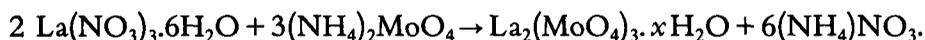


Figure 2. A typical Liesegang ring system of lanthanum molybdate where the rings are overcrowded.

Figure 3. Well-defined ring system with clear void spaces.

luted with distilled water to 100 ml. Sodium silicate solution (density 1.03 g cm^{-3}) titrated with 0.005, 0.01 and 0.02 M values of ammonium molybdate (pH 6-7) was prepared and poured in a set of test tubes (12 cm long, 1.5 cm dia and 7.5 cm high). After the gels were properly set, lanthanum nitrate solution of different molarities (1, 0.8, 0.5, 0.3 and 0.2) were tried as the outer electrolytes with different concentration values of inner electrolyte. Lanthanum nitrate diffuses through the gel medium and the following chemical reaction is expected.



The sparingly soluble product of lanthanum molybdate under certain conditions (table 1) is obtained in the form of rings. The white precipitate of lanthanum molybdate either as bands or rings extends gradually into the gel with different velocities depending on factors like pH of the gel medium, concentrations of outer and inner electrolytes (figure 1).

3. Results and discussion

3.1 Salt effect on the formation of rings

When lanthanum nitrate diffuses into the silica gel charged with ammonium

molybdate a colloidal form of lanthanum molybdate ($\text{La}_2(\text{MoO}_4)_x \cdot x\text{H}_2\text{O}$) in the highly dispersed form is obtained. This solution is a heterogeneous multiphase system of a precipitate of low solubility (Voyutsky 1975). The majority of lanthanum molybdate remaining in the silica gel is due to the acidic nature of the medium, and there is a marked variation in its solubility with hydrogen ion concentration. The distance between successive rings is greatly influenced by the solubility of the precipitating material. Figure 2 represents a particular ring system in a neutral gel medium where the rings are overcrowded, and the boundaries of the rings are not well defined. Without changing inner electrolyte concentration when the concentration of outer electrolyte was increased the rings became more clear and distinguishable (figure 3). In this case the sharpness of the ring is presumed to be due to the increase in acidity of the outer electrolyte solution, and a corresponding reaction product $(\text{NH}_4)\text{NO}_3$ obtained in the medium. Small values of outer electrolyte (0.1 to 0.2 M) for the pH range 6.5-7 could hardly form well-defined rings. In that case a few drops of acidified water added to the outer electrolyte could transform the whole precipitate column completely into well-defined rings. It was found essential to keep a large difference in the concentration of two interacting solutions and this difference is more at enhanced pH. In other words as the MoO_4^{2-} solution in the gel is less acidic, there should be difference in the concentration of interacting ions to form well-defined rings. The solubility in that case is increased by the formation of complex compounds or acid salts or by the amphoteric character of the precipitated compound (Alexeyev 1979). The diffusing electrolyte has a peptizing capacity (Mathur and Ghosh 1958) or can dissolve the precipitate separating out in the form of Liesegang rings. The ring formation for high values of outer electrolyte observed at enhanced pH is found to confirm this behaviour. So a precipitate initially formed redissolves when excess precipitant is added.

3.2 Role of adsorption on the formation of rings

Adsorption is a surface phenomenon and is very important to colloidal systems with a large surface area. There are two types of adsorption, physical and chemical. Physical adsorption is reversible and chemical adsorption is irreversible. The observation of banded precipitate formed by the diffusion of reagents indicates that the zonal structure is due to the adsorption by the precipitate of the solute from the gel until the region next to the precipitate is exhausted of the solute and the reagent is able to diffuse further into the gel before forming fresh band. The idea of the role of adsorption on the formation of ring was introduced for the first time by Bradford (1916). In the present system the clear spaces between the ring appears to be due to the adsorption of molybdate ions by the precipitate of lanthanum molybdate which is in the colloidal form. The adsorption causes changes in the concentration of molybdate ions between the two phases, by the solid phase (ring region) and the so-

lution (void space). The ions tend to become adsorbed and the tendency is greater for anions (MoO_4^{2-} rather than for cations (La^{3+}) (Alexander and Johnson 1950). The primary condition of ring formation is the degree of dispersion of the precipitate and the colloidal state of a substance is a highly dispersed state in which particles are aggregates consisting of numerous molecules. The adsorption effect is usually attributed to polarization (Alexander and Johnson 1950) and may be described as an ion-induced dipole interaction. Thus an ion (MoO_4^{2-} near a material surface of any kind (polar or non-polar) will induce a separation (dipole) in the surface atoms and the induced dipole in turn exerts an attractive force on the ion. If the binding energy (E) is large compared with the thermal energy ($E \gg kT$) the ions will be held at the surface. Various factors determine the magnitude of the binding energy such as charge, size, hydration and the polarisability of the material comprising the interface. Hydration not only increases the size of the ion but reduces the force between an ion and its induced dipole owing to the high dielectric constant of water. Anions (MoO_4^{2-} are usually less hydrated and owing to their large number of electrons per nuclear charge, they are more polarisable than cations (La^{3+}).

Again the radius of ions strongly affect their adsorbability. So they are capable of being attracted by the surface which consists of ions or polar molecules. On the other hand, these ions are hydrated to a smaller extent, hence least obstruction to ionic adsorption. All these reasons are considered to be responsible for the greater adsorption of molybdate ions at the interface and the formation of clear spaces in between consecutive rings.

It is clear from the present studies that the salt products and the property of adsorption of the reaction at certain conditions play a decisive role on the formation of Liesegang rings of lanthanum molybdate in silica gel medium.

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