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Periodic precipitation of cobalt(II) oxinate in agar gel : factors influencing the flocculation

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Abstract. The influence of concentration, ageing and pH of the gel medium on the periodic precipitation of cobalt oxinate in agar gel is reported. The results are explained on the basis of Shinohara's revised flocculation theory. The flocculation value (F) increases with increase in the gel concentration whereas it decreases with increase in ageing and pH of the gel. The raise in temperature of the gel increases the solubility of the sparingly soluble substance and hence the F value. The effect of additives on the periodic precipitation of cobalt(II) oxinate is reported.

Keywords. Periodic precipitation; cobalt oxinate; flocculation value; gel concentration; ageing.

1. Introduction

Many compounds that form insoluble precipitates in a counter diffusion system exhibit the Liesegang (1896) phenomenon in which a series of concentric rings are produced rather than a continuous precipitate. Few quantitative data are available despite over 800 publications on this subject (Stern 1967). The formation of Liesegang rings has been influenced by various factors like concentration of the reactants, concentration, ageing, temperature and pH of the gel medium and the amount of additives present.

We have recently published the experimental conditions for obtaining the Liesegang rings of cobalt(II) oxinate in agar and the influence of the concentration of the reactants on the periodic precipitation (Kanniah *et al* 1981). In this paper the influence of the concentration, ageing, pH and temperature of the gel and the effect of additives on the formation of Liesegang rings of cobalt oxinate are discussed in detail.

2. Theory

The periodic precipitation of cobalt oxinate has been explained on the basis of the revised coagulation theory of Shinohara (1970). As the outer electrolyte—

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cobalt nitrate—diffuses into the gel impregnated with oxine, cobalt oxinate is formed as a sol at the contact plane of the two reactants. This boundary known as sol-front advances spreading the sol region. As more and more outer electrolyte diffuses, the ionic concentration reaches a characteristic value Γ which triggers the flocculation of the sol. Γ is expressed by the equation

$$\Gamma = C_{10}\left[1 - \frac{G(k_1)}{G(k)}\right], \tag{1}$$

where C_{10} is the concentration of cobalt nitrate

$$G(k) = \frac{1}{(2\pi)^{1/2}}\int_0^k \exp\left(-\frac{1}{2}\eta^2\right)d\eta, \tag{2}$$

$$k_1 = k/p \text{ and } p = \frac{x_{n+1}}{x_n}, \tag{3}$$

p is known as the spacing coefficient. x_{n+1} and x_n are the positions of the $(n+1)$th and nth rings from the gel boundary. k is called the front constant which is estimated using the Adair's equation. The concentration of the supersaturated solution of the product (C_{30}) formed just before the formation of sol is given by

$$C_{30} = C_{10}\frac{\exp(-k^2/2)}{(2\pi)^{1/2}kG(k)} \tag{4}$$

The flocculation value F is calculated as

$$F = C_{30} + \Gamma. \tag{5}$$

3. Experimental

3.1. *Effect of gel concentration*

2·178 grams of analytical grade oxine were dissolved in minimum amount of 2N acetic acid. This solution was mixed with hot agar agar solution and the final volume was made up to 300 ml. The pH of the solution was adjusted to 4·25. Thus 1·0% agar agar solution impregnated with 0·05 mole/lit oxine was prepared at 4·25 pH. 50 ml of this solution was poured into a corning tube of 20 mm diameter and allowed to set. After 3 hr 10 ml of 1·031 mole/l cobalt nitrate was taken over the gel. To study the effect of gel concentration of the periodic precipitation of cobalt oxinate, the gel concentration was varied from 0·4% to 2·0%. In all the experiments the concentration of the inner electrolyte and that of the outer electrolyte was kept as 0·05 and 1·031 mole/l respectively.

3.2. *Effect of ageing of the gel*

1% agar agar gel impregnated with 0·05 mole/l oxine was prepared as before. 1·031 mole/l cobalt nitrate was taken over the set gel at different time. The ageing of the gel was varied from 2 to 27 hr.

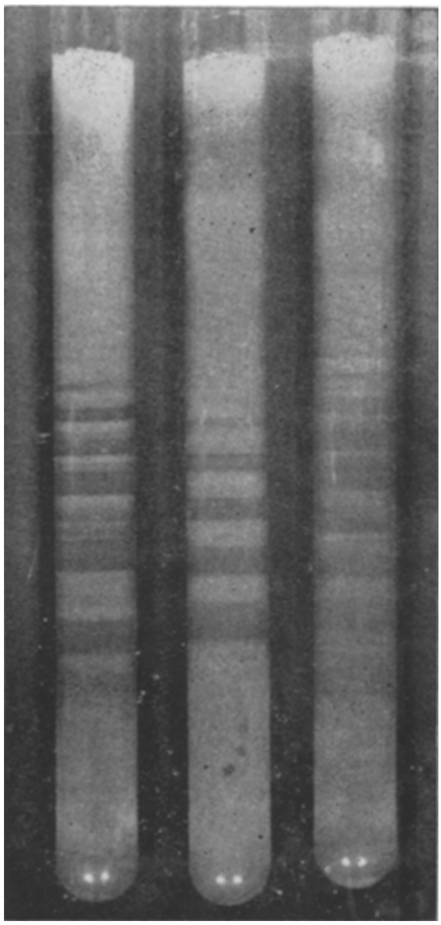

Figure 1. The Liesegang rings of cobalt oxinate in agar gel in presence of additives potassium sodium tartarate, potassium thiocyanate and potassium chloride.

3.3. *Effect of temperature*

The periodic precipitation of cobalt oxinate was normally carried out at room temperature (30° C). The influence of the temperature was studied by keeping the gel at different temperatures. The glass tubes containing the hot gel solution with oxine were immersed in a thermostat kept at the required temperature. The temperature of gel was varied from 30 to 42° C. In all these experiments the concentrations of the gel, oxine and cobalt nitrate was 1%, 0·05 mole/l and 1·031 mole/l respectively.

3.4. *The effect of pH of the gel medium*

Oxine was dissolved in minimum amount of 2N acetic acid and the hot agar agar solution was mixed. The pH of this solution was adjusted with aqueous ammonia to 4·25. Similarly the pH of the gel solution with oxine was varied from 3·7 to 4·7. Oxine is precipitated, when the pH is above 4·7. When the pH was below 3·7 gel set was not observed. The pH of the solution was measured at 60° C. The gel solutions were allowed to set at room temperature (30° C) and cobalt nitrate solution was taken over the set gel after 3 hr. The concentrations of gel, oxine and cobalt nitrate were the same as in the previous experiment.

3.5. *Influence of additives*

To study the effect of additives on the periodic precipitation of cobalt oxinate, suitable additives were taken along with oxine in the gel medium. The amount of additive was varied from 0·001 to 0·026 mole/l. When the gel containing oxine and additive was set, cobalt nitrate was taken as the outer electrolyte. The concentrations of the gel, inner electrolyte and outer electrolyte were kept as 1·0%, 0·05 and 1·031 mole/l respectively. Potassium sodium tartarate, potassium chloride and potassium thiocyanate are the additives taken along with oxine in the gel.

In all the experiments, sharp brown coloured disc-like precipitate rings demarcated by clear void spaces were obtained within a week (figure 1). The interspacing between successive rings increases with the number of ring (n) from the gel boundary. At the lower rings, small crystals of cobalt oxinate were observed. The distance measurements were made with cathetometer. The IBM 1130 computer was used for the calculation of flocculation values using Shinohara's coagulation theory.

4. Results and discussion

4.1. *Effect of concentration of the gel medium*

Matalon and Packter (1955) have established that the gel has a great influence on the periodic precipitation of insoluble salts and that the gel interacts appreciably with the precipitated substance. They have modified Waguer's relation (1950) and derived the following equation:

$$p - 1 = RC_g^m + \frac{B}{C_{10}} \tag{6}$$

where C_g = concentration of the gel; R = a constant and it is a measure of the interaction between the gel and the substance precipitated. B = a constant which is a measure of supersaturation of sparingly soluble substance; m = a constant with integral value; and C_{10} = outer electrolyte concentration.

From the above equation it is very clear that the spacing coefficient (p) will increase with increase in the gel concentration. As the concentration of gel increases the interaction of the gel with the precipitated substance increases. Hence the sol of the sparingly soluble substance is well protected. The stability of the sol increases. Therefore the amount of the outer electrolyte required to flocculate the sol will be more. Thus the flocculation value must increase with increase in the gel concentration (figure 2) leading to an increase in the spacing coefficient (p).

4.2. *Effect of ageing of the gel*

During ageing of the gel the micellae and the intervening capillary spaces become coarser. This will decrease the solubility of cobalt oxinate leading to rapid precipitation. Hence the flocculation value (figure 3) decreases with increase in the ageing of the gel.

4.3. *Effect of temperature*

The increase in temperature of gel leads to a progressive diminution of the total volume of the micellae (Clayton 1932). Hence the pore size increases. This in turn leads to an increase in the diffusion coefficient. Moreover the solubility of

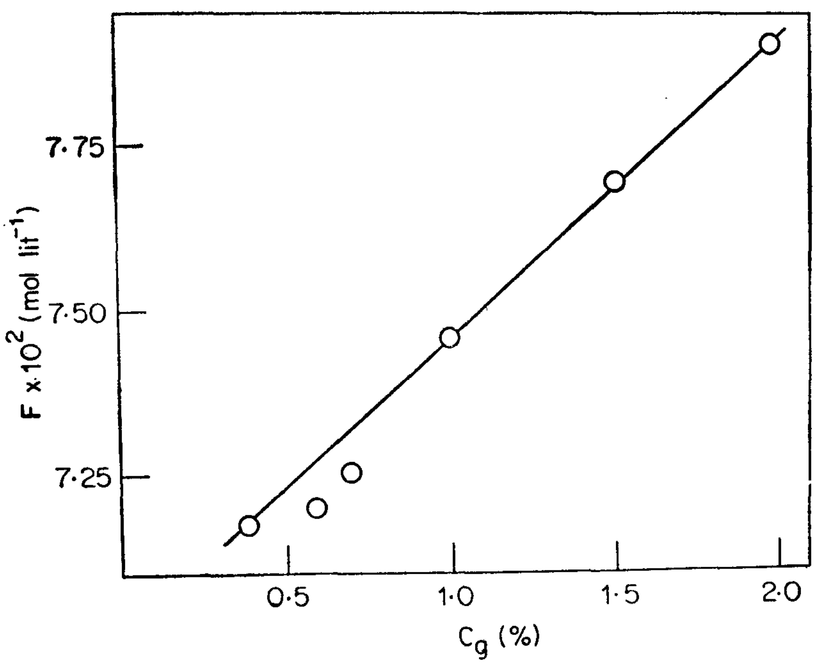

Figure 2. Effect of gel concentration on the flocculation value (F). C_{10} = 1·031 mole/l; C_{20} = 0·05 mole/l.

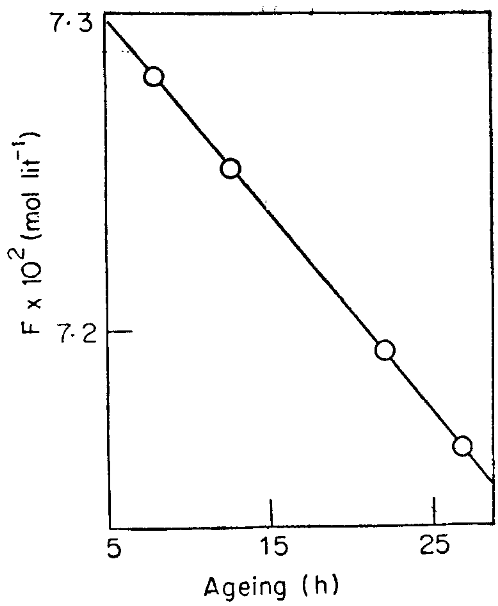

Figure 3. Effect of ageing on the flocculation value (F). $C_{10} = 1 \cdot 031$ mole/l; $C_{20} = 0 \cdot 05$ mole/l., $C_g = 1\%$.

the sparingly soluble product increases with increase in temperature. As the solubility increases the precipitation takes a longer time and hence the rings are formed at greater distances leading to an increase in the spacing coefficient. As the solubility increases, the concentration of the supersaturated solution (C_{30}) formed just before flocculation increases leading to a higher flocculation value (F). Hence increase in temperature of the gel medium increases the flocculation value (table 1).

4.4. *Effect of pH of the gel medium*

The pH of the gel medium plays a predominant role in the periodic precipitation of the sparingly soluble salts (Varma 1953). Cobalt oxinate is soluble in acids. As the pH of the gel medium increases, the solubility decreases leading to a decrease in the spacing coefficient and flocculation value (table 2). The periodic precipitation of cobalt oxinate is observed only in the narrow range of pH 4·3 to 4·0.

4.5. *Effect of additives*

The characteristic features of the periodic precipitation of cobalt oxinate are very much influenced by the presence of additives. The effect of impurities on the periodic precipitation of calcite has been studied by Bugazh and Fraknoy (1961), Gnanam *et al* (1980) and Krishnan *et al* (1981). When potassium sodium tartarate, potassium thiocyanate and potassium chloride are used as additives, the flocculation value increases with increase in the concentration of the impurity. This reveals that solubility of the sparingly soluble product increases with increase in the impurity concentration (McBain 1950). For a particular concentration of

Table 1. Effect of temperature on flocculation value.

C_{10} mole/l	C_{20} mole/l	Temperature °C	p	$F \times 10^2$ mole/l
1·031	0·05	30	1·049	7·038
1·031	0·05	34	1·058	7·380
1·031	0·05	38	1·064	7·426
1·031	0·05	42	1·082	7·897
0·859	0·05	30	1·051	7·035
0·859	0·05	34	1·061	7·126
0·859	0·05	38	1·065	7·212
0·859	0·05	42	1·085	7·658
0·687	0·05	30	1·053	6·997
0·687	0·05	34	1·065	6·983
0·687	0·05	38	1·071	7·093
0·687	0·05	42	1·090	7·425
0·515	0·05	30	1·059	7·067
0·515	0·05	34	1·071	6·881
0·515	0·05	38	1·075	6·926
0·515	0·05	42	1·097	7·227

Table 2. Effect of pH on flocculation value.

pH	C_{10} mole/l	C_{20} mole/l	p	$F \times 10^2$ mole/l
4·05	1·031	0·05	1·101	8·412
4·20	1·031	0·05	1·092	8·167

impurities the flocculation value is the lowest in the case of potassium sodium tartarate (figure 4).

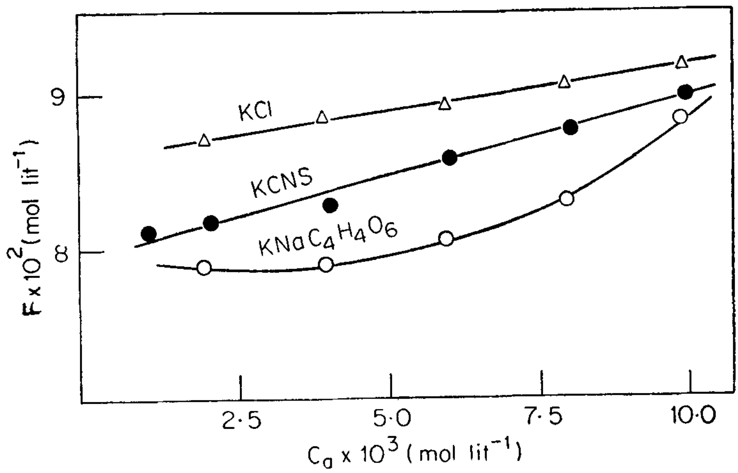

Figure 4. Effect of additives on the flocculation value (F). $C_{10} = 1{\cdot}031$ mole/l; $C_{20} = 0{\cdot}05$ mole/l, $C_g = 1\%$; C_a = concentration of additives.

When excess cobalt nitrate diffuses into a gel impregnated with oxine, a positively charged sol of cobalt oxinate is formed due to the adsorption of excess Co^{2+} ion. In that case the counter-ion plays an important role in flocculating the sol. Among the counter-ions (tartarate, thiocyanate and chloride), the trivalent tartarate will be more effective in flocculating the sol. Hence the flocculation value should be the lowest for a particular concentration of the tartarate. This can also be accounted by the lyotropic order of anions (McBain 1950).

5. Conclusion

The results thus conclusively prove that the concentration, ageing, pH and temperature of the gel have pronounced influence on the flocculation of cobalt oxinate. The flocculation values of different anions are in the lyotropic order.

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