

Periodic precipitation of cobalt (II) oxinate in agar gel : Effect of parasitic electrolytes on flocculation

N KANNIAH, S AMBROSE, F D GNANAM and
P RAMASAMY*

A.C. College of Technology,
Perarignar Anna University of Technology, Madras 600 025, India

MS received 13 March 1981; revised 5 November 1981

Abstract. The experimental conditions for the periodic precipitation of cobalt(II) oxinate in agar agar gel have been extensively studied. When different cobalt salts are taken over the set gel impregnated with oxine, different parasitic electrolytes are formed along with cobalt(II) oxinate. These parasitic electrolytes affect the solubility and hence the periodic precipitation of cobalt(II) oxinate. The effect of the parasitic electrolytes on the flocculation value has been studied on the basis of Shinohara's revised flocculation theory. The spacing law of Jablczynski and the time law have been experimentally verified.

Keywords. Periodic precipitation; cobalt(II) oxinate; parasitic electrolyte; flocculation value; agar gel.

1. Introduction

Periodic precipitation of many sparingly soluble substances has been reported in the literature (Stern 1967). Stern (1954) has reviewed the different theories and factors influencing the periodic precipitation. Shouji Shinohara (1970) has revised the coagulation theory of Dhar and Chatterjee (1922) to explain the periodic precipitation in a quantitative manner. We have recently reported the periodic precipitation of cobalt(II) oxinate in agar agar gel (Kanniah *et al* 1981). In this paper the influence of various parasitic electrolytes on the periodic precipitation of cobalt(II) oxinate has been discussed in detail.

2. Theory

As the outer electrolyte diffuses into the gel impregnated with the inner electrolyte, the inner one itself diffuses in the opposite direction, both obeying Fick's law of diffusion given as

$$\frac{\partial C_1}{\partial t} = D_1 \frac{\partial^2 C_1}{\partial x^2}, \quad (1)$$

* To whom all correspondence should be made.

and

$$\frac{\partial C_2}{\partial t} = D_2 \frac{\partial^2 C_2}{\partial x_2^2}, \quad (2)$$

where C_1 and C_2 are the concentrations of the outer and inner electrolytes and D_1 and D_2 are the diffusion coefficients of the outer and inner electrolytes respectively. The reaction occurs only on the boundary which is a plane perpendicular to the axis of the tube. The outer electrolyte is on one side of the boundary and the inner on the other side. The sparingly soluble reaction product remains as a sol along with the parasitic substance at the boundary, known as 'sol front'. The advancing speed of the sol front is given by

$$v = k (D_{10}/2t)^{1/2}, \quad (3)$$

where D_{10} is the diffusion coefficient of the outer electrolyte at infinite dilution calculated using Nernst equation.

The value of k which controls the behaviour of the sol front is determined by Adair using the boundary condition as

$$D_1 \frac{\partial C_1}{\partial x} + D_2 \frac{\partial C_2}{\partial x} \Big|_{\text{boundary}} = 0. \quad (4)$$

This can be conveniently written as

$$sq \lambda_{1k} + \lambda_{2k} = 0, \quad (5)$$

where

$$q = \frac{C_{10}}{C_{20}}, \quad s = (D_{10}/D_{20})^{1/2},$$

$$C_1 = C_{10} \cdot c_1, \quad C_2 = C_{20} \cdot c_2,$$

$$\lambda_{1k} = \frac{\partial C_1}{\partial x} \Big|_{\text{boundary}},$$

$$\lambda_{2k} = \frac{\partial C_2}{\partial x} \Big|_{\text{boundary}}.$$

If we assume that the diffusion coefficients are constant, then

$$D_1 = D_{10} \text{ and } D_2 = D_{20}.$$

$$c_1 = \frac{G(k) - G(k_1)}{G(k_1)},$$

$$c_2 = \frac{G(k_2) - G(ks)}{\frac{1}{2} - G(ks)},$$

$$\lambda_{1k} = \frac{\exp(-k^2/2)}{\sqrt{2\pi} G(k)},$$

$$\lambda_{2k} = \frac{\exp(-k^2 s^2/2)}{\sqrt{2\pi} [\frac{1}{2} - G(ks)]},$$

(6)

where

$$G(k) = \frac{1}{\sqrt{2\pi}} \int_0^k \exp(-1/2\eta^2) d\eta.$$

$G(k)$ can also be given in terms of the error function

$$G(k) = \frac{1}{2} \operatorname{erf}(k/\sqrt{2}),$$

since

$$\operatorname{erf}(k) = \frac{2}{\sqrt{\pi}} \int_0^k \exp(-\eta^2) d\eta.$$

Substituting in (5)

$$sq \frac{\exp(-k^2/2)}{G(k)} = \frac{\exp(-k^2 s^2/2)}{1/2 - G(ks)}, \quad (7)$$

$$sq \frac{\exp(-k^2/2)}{\operatorname{erf}(k/\sqrt{2})} = \frac{\exp(-k^2 s^2/2)}{1 - \operatorname{erf}(ks/\sqrt{2})}$$

using error function

$$= \frac{\exp(-k^2 s^2/2)}{\operatorname{erfc}(ks/\sqrt{2})}. \quad (8)$$

Equation (7) is known as Adair's equation. The front constant k is calculated for different values of q using (7).

The sol front advances by forming sol of the sparingly soluble reaction product. The substance is in a state of supersaturated solution, before the formation of sol. The concentration of this supersaturated solution just before the formation of the sol, known as the reduced concentration (C_{30}) is given by

$$C_{30} = C_{10} \frac{\exp(-k^2/2)}{\sqrt{2\pi} k G(k)}. \quad (9)$$

From the above equation it can be noted that the reduced concentration (C_{30}) is constant everywhere, though the speed of the sol front slows down gradually as it advances.

As the diffusion proceeds the concentration of the outer electrolyte varies with the distance from the largest value (C_{10}) at the gel boundary to zero at the sol front. The flocculation of the sol is caused by the ions of the outer electrolyte and the parasitic electrolyte formed during the sol formation. As the ionic concentration of the outer electrolyte reaches a value F which is characteristic of the sol, flocculation occurs. This characteristic value F can be defined from (6) as

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

where

$$k_1 = k/p \text{ and } p = x_{n+1}/x_n. \quad (11)$$

2.1. Flocculation value

The sol of the sparingly soluble reaction product is formed with the concomitant formation of a soluble parasitic electrolyte which produces ions on ionization. The influence of the parasitic ions depends on the valency of the outer electrolyte and the parasitic electrolyte. That is whether the outer electrolyte and the parasitic electrolyte are monovalent, divalent or trivalent in action. The flocculation value of the sol is given by $F = C_{30} + F$.

3. Experimental

1.3068 gram of analar oxine (8-quinolinol) was just dissolved in 2*N* acetic acid solution. To this solution, 25% ammonia solution was added drop by drop until a faint but permanent turbidity was obtained. A few drops of 2*N* acetic acid were added to produce a clear solution. The pH of this solution was adjusted to 4.25. This oxine solution was mixed with agar agar gel solution and the gel solution with oxine was made upto 300 ml with hot double distilled water. This gave 0.03 M oxine in 1% agar agar. Similarly 1% agar agar solutions containing oxine of concentrations 0.06 M and 0.05 M were prepared. 50 ml of these clear solutions were poured into a corning tube of 20 mm diameter and allowed to set. After 3 hr 10 ml of cobalt(II) sulphate solutions of 1.031, 0.859, 0.687, 0.515 and 0.344 M concentrations were carefully taken over the set gel.

The experiments were carried out with cobalt(II) chloride and cobalt(II) bromide as the outer electrolytes. In all these cases the concentrations of the outer electrolyte were 1.031, 0.859, 0.687, 0.515 and 0.344 and the concentrations of the inner electrolyte were 0.06 M, 0.05 M and 0.03 M. The experiments were carried out at room temperature (30°C). Sharp brown coloured disc like precipitate rings demarcated by clear void spaces were obtained (figure 1). The distance measurements were made with a cathetometer. The IBM 1130 computer was used for the calculation of flocculation values using Shinohara's revised coagulation theory.

4. Results

4.1. Verification of time law

According to Shinohara the movement of the sol front can be expressed as

$$x_n = k (2D_{10} t)^{1/2},$$

$$\text{or } \frac{x_n}{\sqrt{t_n}} = k \sqrt{2D_{10}} = K.$$

K is known as the velocity constant. For a given pair of concentrations of the inner and outer electrolytes, K is found to be a constant, thus verifying the time law. The velocity constant increases with the increase in the concentration of the outer electrolyte. Figure 2 shows the dependence of K on the concentrations of CoSO_4 , CoCl_2 and CoBr_2 , for the same inner electrolyte concentration.

4.2. Verification of the spacing law

According to Jablczyński's (1923) spacing law

$$x_n = x_0 p^n,$$

$$p = \frac{x_{n+1}}{x_n}$$

where p is known as the spacing coefficient, x_{n+1} and x_n are the positions of the $(n+1)$ th and n th rings from the gel boundary and x_0 is a constant. Figure 3 shows a plot of the numerical order of the ring (n) against $\log x_n$ for the same

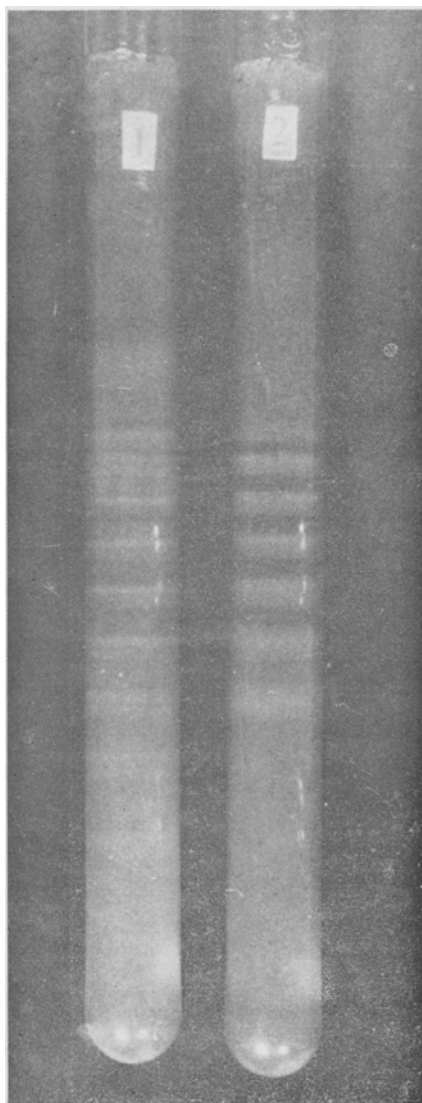


Figure 1. Periodic precipitation of cobalt(II) oxinate in agar agar gel. The concentration of oxine is 0.05 mole/litre. The concentration of cobalt sulphate is 1.031 mole/litre and 0.515 mole/litre for tubes 1 and 2 respectively.

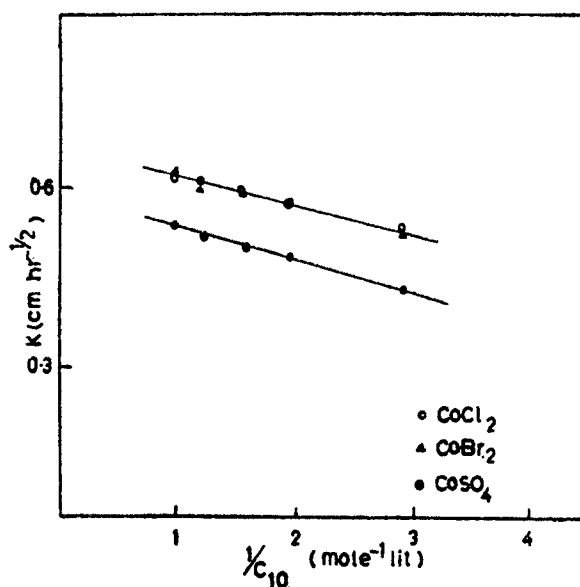


Figure 2. The dependence of K on the concentration of the outer electrolytes.

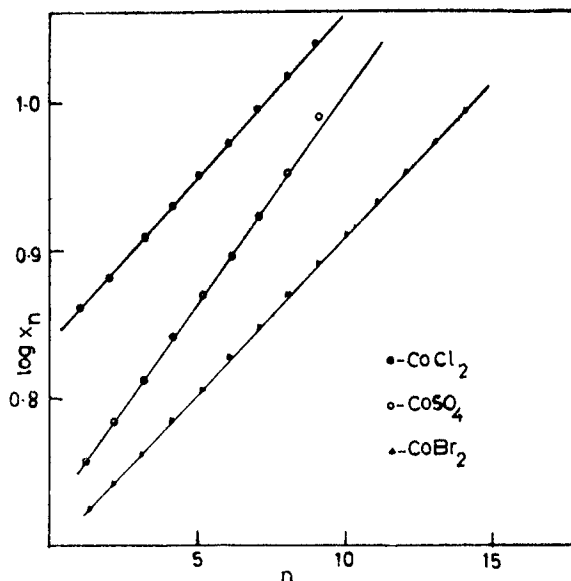


Figure 3. Verification of Jablczynski's spacing law.

concentration of the different outer electrolytes. The linear variation verifies the spacing law of Jablczynski.

4.3. The dependence of spacing coefficient on the concentrations of the outer electrolytes

The spacing coefficient $p = x_{n+1}/x_n$ decreases with increase in the concentration of the outer electrolyte, for a given inner electrolyte concentration C_{10} . This

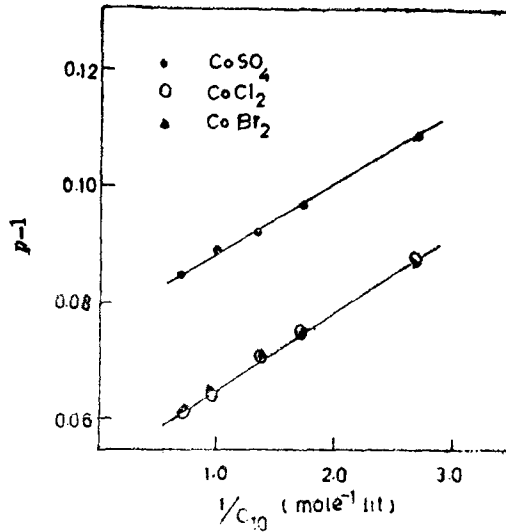


Figure 4. The dependence of spacing coefficient on the outer electrolyte concentration.

observation is true for all the outer electrolytes taken over the set gel. The dependence of the spacing coefficient on the outer electrolyte concentration has been represented in figure 4.

4.4. Calculation of flocculation value

The reduced concentration of the sol is calculated using the equation,

$$C_{30} = C_{10} \frac{\exp(-k^2/2)}{\sqrt{2\pi kG(k)}}.$$

The characteristic concentration of the outer electrolyte, Γ required to initiate flocculation is calculated using the equation

$$\Gamma = C_{10} \frac{G(k) - G(k_1)}{G(k)}.$$

Then the flocculation value of the sol

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

The flocculation values are computed for various concentrations of the different outer electrolytes. Table 1 shows the computed values of C_{30} , Γ , F and $G(k)$, when CoSO_4 is used as the outer electrolyte. Tables 2 and 3 show the corresponding values for cobalt chloride and cobalt bromide respectively. The computed flocculation value is the highest when cobalt sulphate is used as the outer electrolyte. The concentration of the inner electrolyte being constant, the flocculation values of cobalt(II) chloride and cobalt(II) bromide are almost equal for a particular concentration of the outer electrolyte. As the concentration of the outer electrolyte decreases, Γ value decreases for all the three outer electrolytes, whereas the C_{30} value increases. Hence the flocculation value F is a constant for a given inner electrolyte concentration. As the concentration of the inner

Table 1. Estimated values of C_{∞} , k , Γ and F : $\text{CoSO}_4 + 2\text{C}_9\text{H}_7\text{ON} \rightarrow \text{Co}(\text{C}_9\text{H}_6\text{ON})_2 + \text{H}_2\text{SO}_4$, $s = 0.9673$.

C_{10} mole/lit	C_{30} mole/lit	Observed			Estimated					F/C_{30}	
		$q = C_{10}/C_{30}$	p	x/\sqrt{t} cm hr ^{-1/2}	k	$G(k)$	k_1	$\Gamma \times 10^2$ mole/lit	$C_{\infty} \times 10^2$ mole/lit		$F \times 10^2$ mole/lit
1.031	0.06	17.183	1.085	0.473	1.913	0.472	1.763	2.419	7.304	9.723	162.1
0.859	0.06	14.317	1.090	0.468	1.837	0.467	1.685	2.372	7.390	9.762	162.7
0.687	0.06	11.450	1.092	0.454	1.743	0.460	1.596	2.180	7.492	9.672	161.2
0.515	0.06	8.583	1.097	0.409	1.618	0.447	1.475	1.990	7.667	9.657	161.0
0.344	0.06	5.733	1.110	0.380	1.438	0.425	1.295	1.817	7.986	9.803	163.4
1.031	0.05	20.620	1.066	0.512	1.987	0.477	1.864	1.666	6.031	7.697	153.9
0.859	0.05	17.180	1.073	0.490	1.913	0.472	1.783	1.714	6.086	7.800	156.0
0.687	0.05	13.740	1.079	0.458	1.820	0.466	1.687	1.685	6.170	7.855	157.1
0.515	0.05	10.300	1.085	0.424	1.697	0.455	1.564	1.591	6.300	7.891	157.8
0.344	0.05	6.880	1.095	0.397	1.520	0.436	1.388	1.446	6.524	7.970	159.4
1.031	0.03	34.367	1.065	0.536	2.186	0.486	2.053	1.196	3.552	4.748	158.3
0.859	0.03	28.633	1.072	0.510	2.116	0.483	1.974	1.248	3.574	4.822	160.7
0.687	0.03	22.900	1.077	0.492	2.029	0.479	1.884	1.123	3.600	4.723	157.4
0.515	0.03	17.167	1.081	0.480	1.913	0.472	1.770	1.144	3.648	4.793	159.7
0.344	0.03	11.467	1.093	0.421	1.743	0.460	1.595	1.100	3.745	4.845	161.5

Table 2. Estimated values of C_{30} , k , Γ and F : $\text{CoCl}_3 + 2\text{C}_6\text{H}_5\text{ON} \rightarrow \text{Co}(\text{C}_6\text{H}_5\text{ON})_2 + 2\text{HCl}$, $s = 1.1734$.

C_{10} mole/lit	C_{30} mole/lit	Observed		x/\sqrt{t} cm hr ^{-1/2}	k	$G(k)$	k_1	Estimated		$F \times 10^3$ mole/lit	F/C_{30}
		$q = C_{10}/C_{30}$	p					$\Gamma \times 10^3$ mole/lit	$C_{30} \times 10^3$ mole/lit		
1.031	0.06	17.183	1.062	0.573	1.927	0.473	1.815	1.694	7.045	8.739	145.7
0.859	0.06	14.317	1.065	0.523	1.859	0.468	1.741	1.647	7.077	8.724	145.4
0.687	0.06	11.450	1.071	0.507	1.763	0.461	1.645	1.632	7.143	8.775	146.3
0.515	0.06	8.583	1.076	0.503	1.640	0.450	1.524	1.518	7.269	8.778	146.3
0.344	0.06	5.733	1.088	0.430	1.465	0.429	1.347	1.407	7.472	8.879	148.0
1.031	0.05	20.620	1.052	0.600	1.999	0.478	1.895	1.349	5.839	7.188	143.8
0.859	0.05	17.180	1.057	0.589	1.928	0.473	1.824	1.298	5.855	7.153	143.1
0.687	0.05	13.740	1.060	0.556	1.837	0.467	1.733	1.242	5.910	7.152	143.0
0.515	0.05	10.300	1.065	0.537	1.717	0.457	1.612	1.182	5.994	7.176	143.5
0.344	0.05	6.880	1.077	0.477	1.545	0.439	1.435	1.134	6.134	7.268	145.4
1.031	0.03	34.367	1.059	0.618	2.190	0.486	2.068	1.074	3.513	4.587	152.9
0.859	0.03	28.633	1.061	0.603	2.123	0.483	2.001	1.035	3.508	4.543	151.4
0.687	0.03	22.900	1.063	0.599	2.039	0.479	1.918	0.979	3.507	4.486	149.5
0.515	0.03	17.167	1.073	0.565	1.927	0.473	1.796	1.008	3.519	4.527	150.9
0.344	0.03	11.467	1.075	0.540	1.762	0.461	1.639	0.864	3.577	4.441	148.0

Table 3. Estimated values of C_{90} , k , Γ and F : $\text{CoBr}_2 + 2\text{C}_9\text{H}_9\text{ON} \rightarrow \text{Co}(\text{C}_9\text{H}_9\text{ON})_2 + 2\text{HBr}$, $s = 1.1798$.

C_{10} mole/lit	Given C_{90} mole/lit	$q = C_{10}/C_{90}$	Observed		x/\sqrt{t} cm hr ^{-1/2}	k	$G(k)$	k_1	Estimated		$F \times 10^3$ mole/lit	F/C_{90}
			P	P					$\Gamma \times 10^2$ mole/lit	$C_{90} \times 10^3$ mole/lit		
1.031	0.06	17.183	1.063	1.063	0.574	1.927	0.473	1.813	1.728	7.045	8.773	146.2
0.859	0.06	14.317	1.066	1.066	0.550	1.854	0.468	1.739	1.679	7.077	8.756	145.9
0.687	0.06	11.450	1.069	1.069	0.545	1.762	0.461	1.648	1.586	7.143	8.729	145.5
0.515	0.06	8.583	1.076	1.076	0.480	1.640	0.450	1.524	1.518	7.260	8.778	146.3
0.344	0.06	5.733	1.087	1.087	0.435	1.465	0.429	1.348	1.368	7.472	8.840	147.3
1.031	0.05	20.620	1.051	1.051	0.592	1.999	0.478	1.902	1.249	5.839	7.088	141.8
0.859	0.05	17.180	1.055	1.055	0.565	1.928	0.473	1.827	1.257	5.855	7.113	142.2
0.687	0.05	13.740	1.062	1.062	0.518	1.837	0.467	1.730	1.281	5.910	7.191	143.8
0.515	0.05	10.300	1.066	1.066	0.500	1.717	0.457	1.611	1.195	5.994	7.189	143.8
0.344	0.05	6.880	1.085	1.085	0.435	1.545	0.439	1.424	1.258	6.134	7.392	147.8
1.031	0.03	34.367	1.061	1.061	0.626	2.190	0.486	2.064	1.104	3.513	4.627	154.2
0.859	0.03	28.633	1.063	1.063	0.592	2.123	0.483	1.997	1.074	3.508	4.582	152.7
0.687	0.03	22.900	1.067	1.067	0.588	2.039	0.479	1.911	1.043	3.507	4.550	151.7
0.515	0.03	17.167	1.068	1.068	0.578	1.927	0.473	1.804	0.939	3.519	4.458	148.6
0.344	0.03	11.467	1.083	1.083	0.518	1.762	0.461	1.627	0.958	3.577	4.535	151.2

electrolyte decreases, the flocculation value decreases appreciably for a particular outer electrolyte concentration. Hence the concentration of the inner electrolyte plays a major role in determining the flocculation value. F/C_{20} is a constant for a particular concentration of the inner electrolyte.

5. Discussion

5.1. Dependence of the velocity constant

The diffusion coefficients of CoBr_2 ($1.2904 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$) and CoCl_2 ($1.2763 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$) are almost equal. The velocity of the sol (v) front is the same for both the outer electrolytes. Hence the values of the velocity constant do not show any appreciable difference. As the diffusion coefficient of CoSO_4 is very low ($0.8674 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$) the velocity of the sol front and hence the velocity constant are less than those for CoBr_2 and CoCl_2 .

5.2. Effect of concentration of the outer electrolyte on spacing coefficient

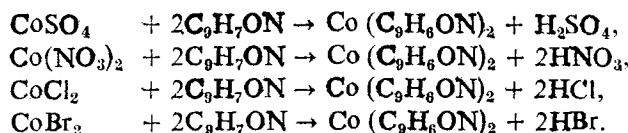
The relation between the spacing coefficient (p) and the concentration of outer electrolyte (C_{10}) is given by Matalon and Packter's (1955) equation

$$(p - 1) = A + B/C_{10},$$

where A and B are constants. The plot of $(p - 1)$ versus $1/C_{10}$ gives a straight line (figure 4). The slope of the line gives B which is directly dependent on supersaturation. Since the same straight line represents both CoCl_2 and CoBr_2 the supersaturation and the solubility of cobalt oxinate are the same when HCl and HBr are formed as the parasitic electrolytes. The slope of this line is greater than that of the straight line for CoSO_4 . This means that the degree of supersaturation is less when CoSO_4 is the outer electrolyte. In other words the presence of H_2SO_4 as the parasitic electrolyte increases the solubility of cobalt(II) oxinate.

5.3. Flocculation value

When the outer electrolyte is allowed to diffuse into the gel impregnated with oxine, cobalt oxinate is formed as a sol with the concomitant formation of a soluble parasitic electrolyte.



These parasitic electrolytes have different characteristics and produce different ions on ionization. They will have different effect on the flocculation of the positively charged cobalt oxinate sol formed due to the adsorption of excess of cobalt ion. The flocculation of the sol is caused by the counter ions supplied by the outer electrolyte and the parasitic electrolyte. So it may appear that the divalent anion—sulphate—should be more effective in flocculation than the monovalent anions, chloride and bromide. But the analysis of the tables 1, 2 and 3 shows that the flocculation value of sulphate is greater than that of others. The concentration of the supersaturated solution (C_{30}) of cobalt oxinate formed before the sol forma-

tion is greater for CoSO_4 . In other words only after the attainment of this value C_{30} , the sol formation is possible. More outer electrolyte has to diffuse to satisfy this condition. It is very clear from the foregoing arguments, that the presence of parasitic electrolyte H_2SO_4 increases the solubility of cobalt oxinate. It takes longer to exceed the solubility product. Hence the flocculation value (F) and the spacing coefficient (p) are greater than those for other outer electrolytes. This result is in accordance with Wagner's (1950) theoretical prediction. Similar results have been reported for calcite (Gnanam *et al* 1980) and silver chromate (Verma and Ghosh 1953).

We have recently reported the periodic precipitation of cobalt oxinate formed by diffusing cobalt(II) nitrate (Kanniah *et al* 1981) into agar gel containing oxine. The computed values of the concentration of the supersaturated solution (C_{30}) are identical in the case of cobalt bromide, chloride and nitrate. Hence the parasitic electrolytes HBr , HCl and HNO_3 affect the solubility of cobalt oxinate to the same extent. Until the formation of the sol the conditions are identical in the case of cobalt nitrate, chloride and bromide. However a close analysis of the flocculation values will reveal the fact that the flocculation values are in the following order :



Hence the flocculating capacity is in the reverse order.

6. Conclusion

The periodic precipitation of cobalt(II) oxinate obtained by diffusing different electrolytes into the agar agar gel impregnated with oxine reveals the influence of the parasitic electrolyte on the solubility of cobalt(II) oxinate. The flocculating capacities of different anions are compared.

Acknowledgement

This work is supported by CSIR and UGC, New Delhi. One of the authors (NK) thanks UGC for the award of a fellowship.

References

- Dhar N R and Chatterjee A C 1922 *Kolloid. Z.* **31** 15
- Gnanam F D, Krishnan S, Ramasamy P and Laddha G S 1980 *J. Colloid Interface Sci.* **73** 193
- Jablczynski K 1923 *Bull. Soc. Chim. France* **33** 1952
- Kanniah N, Gnanam F D and Ramasamy P 1981 *J. Colloid Interface Sci.* **80** 377
- Matalon R and Packter A 1955 *J. Colloid Sci.* **10** 46
- Shouji Shinohara 1970 *J. Phys. Soc. Jpn.* **29** 1073
- Stern K H 1954 *Chem. Rev.* **53** 79
- Stern K H 1967 *Bibliography of Liesegang rings* (USA : National Standards)
- Verma K K and Ghosh G 1953 *Kolloid-Z.* **133** 32
- Wagner C 1950 *J. Colloid Sci.* **5** 85