THE DISSOLUTION OF CALCIUM OXALATE IN THE PRESENCE OF SOME NATURAL PRODUCTS

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The kinetics of dissolution of calcium oxalate crystals were investigated conductimetrically in several calcium oxalate undersaturated solutions. Over a range of relative undersaturation (0.3 - 0.8) and at 37 °C the process appears to follow a surface controlled dissolution mechanism. The presence of trace amounts of natural products from medicinal plants in the undersaturated solution inhibits the dissolution process. Application to a kinetic Langmuir-type model suggests that adsorption of the natural product at the active dissolution sites is the cause of the reduction in the dissolution rates.

INTRODUCTION

The precipitation and dissolution of sparingly soluble calcium salts are of interest due to its widespread and universal applicability[1,2]. Oxalates are the main inorganic components in pathological deposits and play a key role in the formation of kindney stones[3,4]. Precipitation and dissolution studies of calcium oxalate and the influence caused on such processes by foreign substances, are of great interest in view of their potential application in the urolithiasis therapy [6,7]. In the present work, an attempt is made to study the kinetics of dissolution of calcium oxalate in aqueous solutions by a conductivity method. The rates of dissolution of calcium oxalate have been studied as a function of different parameters such as undersaturation, amount of seeds, hydrodynamics and presence of trace quantities of extracts from some medicinal plants.

EXPERIMENTAL

Calcium chloride and sodium oxalate solutions were prepared using chemicals of pure grade reagents with triply deionized water. Calcium oxalate monohydrate seed crystals prepared by mixing 0.01 mol dm^{-3} solutions of calcium chloride and sodium oxalate at 70 °C, were aged for at least one month before use.

Dissolution experiments were made in Pyrex glass vessels of approximately 300 ml capacity. The solutions were maintained at an appropriate temperature by circulating thermostatted water through the corresponding containers ($\pm$ 0.1 °C). Working solutions were always magnetically stirred, and nitrogen gas was bubbled throughout the experiment.

The dissolution reaction was initiated by the introduction of a weighted amount of calcium oxalate monohydrate seed crystals in the undersaturated solution. Dissolution was followed through conductimetric measurements by means of a Tacucell Conductimeter CD 6N.

RESULTS   AND   DISCUSSION

The concentrations of ionic species in the solutions were calculated from mass-balance and electroneutrality expressions as described previously[8]. Activity coefficients were calculated from the extended from of the Debye-Hückel equation proposed by Davies[9].

For many sparingly soluble salts, M_aA_b, the rate of dissolution, normalized for seed surface area can be expressed by the equation[10].

$$R = d\,[M_aA_b]\ /\ dt\ =\ ks\ \sigma^n \qquad (1)$$

in which k is the dissolution rate constant, s is proportional to the number of dissolution sites available on the seed crystals, n is the effective order of reaction and σ is the relative undersaturation. The relative undersaturation, σ, may be expressed by the equation.

$$\sigma = (II_0^{1/2} - II^{1/2}) / II_0^{1/2} \qquad (2)$$

in which II is the molar concentration product of calcium oxalate, $[Ca^{2+}][ox^{2-}]$, in the solutions and II_0 the solubility value at the same ionic strength (0.15 mol dm^{-3} in the present work) and the conditional solubility product, K_{so}, was 2.2 x 10^{-9} mol^2 dm^{-6} [11].

The results of dissolution experiments from pure solutions are summarized in table (1) and the time plots of the amount of calcium oxalate dissolved are shown in Fig. (1). Assuming, as a first approximation simple spherical or cubic particles, corrections were made for changes in surface area during the dissolution reactions by introducing a factor $(w_i / w_t)^{2/3}$, where w_i and w_t are the masses of solid phase present initially and at time t, respectively. It can be seen in table (1) that the rates of dissolution were proportional to the mass of seed crystals used to initiate the reactions. Logarithmic plots of the rate R in equation (1) yielded straight lines that allowed the evaluation of the apparent order n. Fig. (1) presents logarithmic plots corresponding to kinetics of dissolution of calcium oxalate monohydrate seed crystals. As can be seen, an apparent order of n ≈ 2 was obtained which confirms a surface-controlled mechanism in the range of relative undersaturation 0.3 > σ > 0.8. The suggestion of a predominantely surface-controlled process may also be supported by the observed independence of the experimental rate of dissolution changes in fluid dynamics, as shown in table (1) compare expts. [(39), (41) and (50), (51)]. It has

been observed [12] that there was a change with mechanism of the dissolution of calcium oxalate monohydrate from diffusion to surface controlled reactions as the degree of saturation was decreased.

The crystallization rates of calcium oxalate[13-15] and divalent metal ion salts in general[16-18] are greatly inhibited by added substances. The possible inhibitory effects of some water extracts from medicinal plants on the dissolution rate of calcium oxalate were investigated. The rate of dissolution was studied in the presence of sugar cane and cymbopogon proximus. Table (2) summarizes the data for both additives, each experiment was made in duplicate or triplicate for certainties. From the rate profiles shown in Fig. (3), the dissolution rates of calcium oxalate in the presence of some water extracts from medicinal plants (sugar cane and cymbopogon) decrease with successive additions of additives. It can be seen that the concentrations as low as 6.2×10^{-4} gm dm^{-3} for each additive (expts 64 and 75) reduced the dissolution rates by as much as 79.02% and 66.91%, compared to that in pure solution at the same relative undersaturation in the presence of saccharum and cymbopogon, respectively. 10^{-6} mol dm^{-3} phosphonate concentrations have been shown to reduce the rate of dissolution of magnesium fluoride by as mush as 50%[19]. The order of the degree of inhibition is saccharum > cymbopogon proximus at the relative undersaturation, $\sigma = 0.7$. As the concentration of additive molecules increases, the active dissolution sites on the crystal surfaces are blocked through adsorption and the rate of crystal dissolution decreases.

On the assumption that the decreased dissolution rate reflects the adsorption of extractions at active dissolution sites, the influence of both inhibitors can be interpreted in terms of a Langmuir-type equation[20]. The reduction in dissolution

Table (1) : Dissolution of calcium oxalate monohydrate crystals at 37°C

Expt. No	T_{ca} (10^{-5} mol dm^{-3})	10σ	Seed (mg)	Rate (10^{-6} mol.min^{-1} m^{-2})
39	1.126	8	15	1.614
40	1.689	7	15	1.254
41	2.252	6	15	1.110
24 - 47	2.815	5	5 - 30	0.558
48	3.378	4	20	0.323
49	3.941	3	27	0.184
50	1.126	8	15	1.622
51	2.252	6	15	1.116

* $T_{ca.}$ / $T_{ox.}$ = 1, stirring speed 200 r.p.m., r.p.m., with 300 r.p.m. for expt. (50) and (51).

Table (2) : Effect of additives on the rates of dissolution of calcium oxalate monohydrate crystals at $\sigma = 0.7$.

Exp. No.	Additive (10^{-4} gm dm^{-3})		Rate (10^{-6} molmin^{-1}m^{-2})	% Inhibition
40	-	-	1.254	-
55	s	0.31	1.122	10.52
56	s	0.46	1.013	19.21
57	s	0.62	0.941	24.96
58	s	0.93	0.874	30.30
59	s	1.24	0.754	39.87
60	s	1.85	0.634	49.44
61	s	2.47	0.545	56.53
62	s	3.09	0.452	63.95
63	s	4.33	0.359	68.50
64	s	6.18	0.263	79.02
65	s	7.42	0.215	82.85
66	s	9.27	0.177	85.88
67	s	12.36	0.161	87.16
68	c	0.18	1.178	6.06
69	c	0.59	1.065	15.07
70	c	0.95	0.992	20.89
71	c	1.51	0.885	29.43
72	c	2.20	0.775	38.20
73	c	3.18	0.632	49.60
74	c	4.72	0.513	59.09
75	c	6.20	0.415	66.91
76	c	8.38	0.330	73.68
77	c	11.02	0.275	78.70
78	c	13.35	0.204	83.73

S : Saccharum.
C : Cymbopogon.

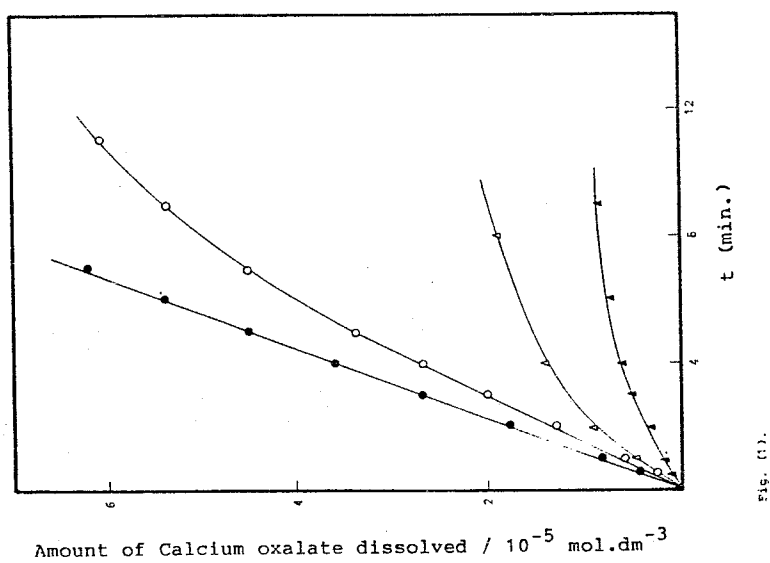Amount of Calcium oxalate dissolved / 10^{-5} mol.dm^{-3}

Fig. (1) : Plots of amount of calcium oxalate dissolved against time : expt 39 (o),
40 (O), 41 (△) and 48 (▲).
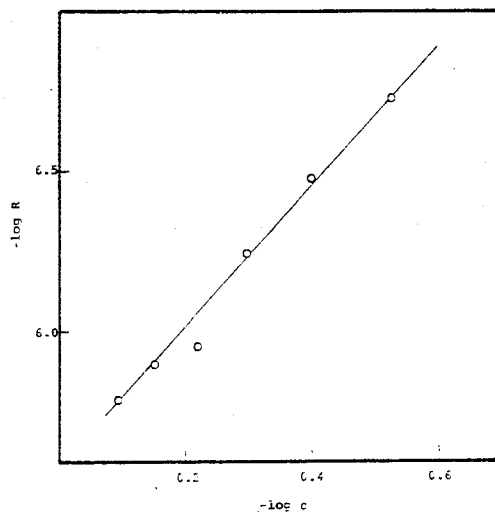

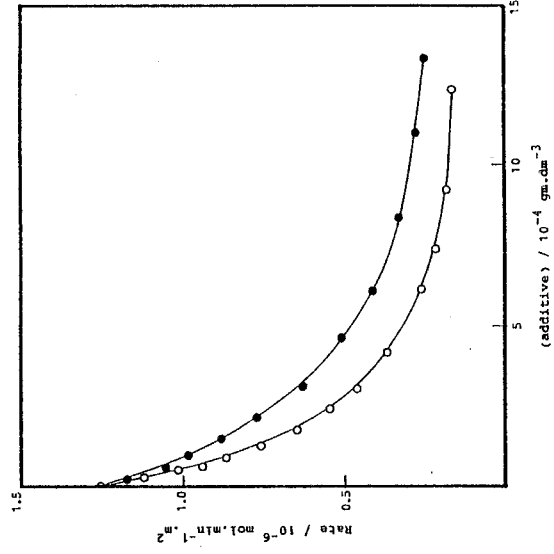Fig. (2) : Plots of - log R against - log σ for dissolution of calcium oxalate.

Fig. (3) : Plots of rates of dissolution against [additive] at undersaturation ($\sigma = 0.7$), (O) saccharum and (O) cymbopogon.
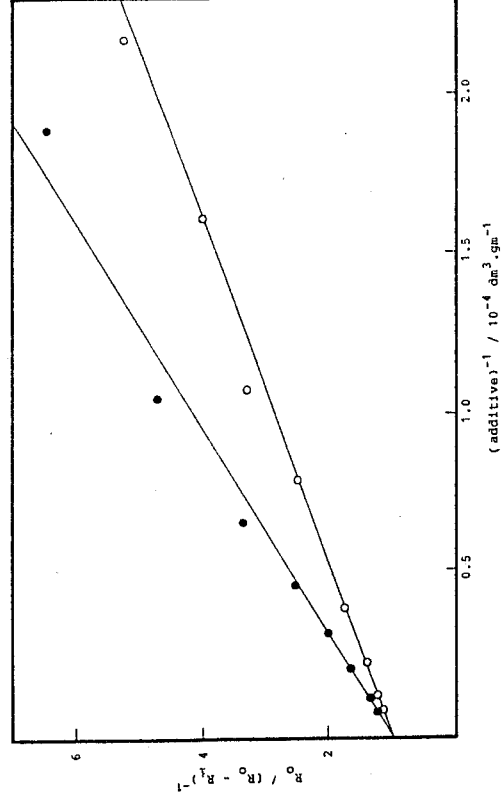
Fig. (4) : Plots of $R_O (R_O - R_i)^{-1}$ against [additive]$^{-1}$ saccharum (o) and cymbopogon proximus (o).

rate then reflects the increased crystal surface area covered by the adsorbed inhibitor molecules. If R_0 and R_i are the rates of dissolution in the absence and presence of inhibitors, respectively, the Langmuir equation requires a linear relationship between the reciprocal of the relative reduction in rate, $(R_0 / R_0 - R_i)$, and the reciprocal of the inhibitor concentration[20], Fig. (4) confirms the applicability of this interpretation for both extracts at the same relative undersaturation. The values of the adsorption affinity constants K_L are 5.32×10^3 L gm^{-3} and 3.45×10^3 L gm^{-1} for saccharum and cymbopogon proximus, respectively. These values reflect the high adsorption affinity at the same relative undersaturation ($\sigma = 0.7$) in order saccharum > cymbopogon proximus.

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