

NOTE

**Alkaline Earth Metal Complexes: Reactions of Calcium Ions
with Common Plant Acids**

BASABI MAHAPATRA (CHOWDHURY)*, SHAIL BALA and BARUN KUMAR MISHRA
*Department of Chemistry
Patna University, Patna-800 020, India*

Calcium complexes of malonic, succinic and glutaric acids have been investigated by conductometric titrations. The data indicated the formation of binary 1:1 and 1:2 calcium malonate, 1:1, 1:2 and 1:3 calcium succinate and glutarate complexes.

Calcium phosphate constitutes an important bio-inorganic compound. Stones, that are formed in the kidneys of animal systems, contain calcium phosphate together with calcium oxalate which are highly insoluble compounds. Our primary aim had been to find out the possibilities of dissolving out the urinary stones by the application of some naturally occurring compounds that would be physiologically non-toxic to the animal system. In this paper the complexes with plant acids are reported on the basis of conductometric evidences. We have isolated 1:1 and 1:2 calcium malonate, 1:1, 1:2 and 1:3 calcium succinate and glutarate complexes. Some complexes of calcium phosphate with naturally occurring citric, malic and tartaric acids have been reported¹.

Suspensions of known weights of calcium orthophosphate (tribasic) in 100 mL of deionised conductivity water, were titrated conductometrically against the standard aqueous solutions of malonic, succinic and glutaric acids. All the acid solutions were prepared in deionised conductivity water. All the titrations were carried out on a direct reading conductivity meter (Systronics type 303), with a conductivity cell of black platinized electrodes. The instrument was calibrated with standard KCl solution. After each addition of the titrant, a time period of 3 min for stirring followed by 1 min for settling down, was allowed before taking the reading.

The solid complexes were isolated by the general method of interaction of suspensions of calcium phosphate in water with excess of the solutions of the acids, till clear solutions could be obtained. A little more of acid solutions were added to keep the acid in slight excess. The clear solutions thus obtained were filtered and the filtrates concentrated on a water bath for crystallisation. The white

*For correspondence: Department of Chemistry, Patna Women's college, Bailey Road, Patna-800 001, India.

compounds were obtained upon cooling the concentrates and white crystalline compounds were separated out. These compounds were filtered, washed well with cold distilled water and dried in an air oven at 110°C. Melting and decomposition temperatures of the compounds were recorded.

The colour, solubility, decomposition temperatures and elemental analysis results are given in Table-1. The complex with glutaric acids could not be isolated.

TABLE-1

Compound	Colour	Aqueous solubility	Decomp. temp. (°C)	Analytical results % Req. (Found)		
				Ca	C	H
Calcium phosphato malonate	white	modrately soluble	340	23.16 (23.33)	12.1 (10.9)	1.50 (2.60)
Calcium phosphato succinate	white	moderately soluble	340	21.97 (19.83)	11.2 (11.2)	2.20 (4.82)

The curve for calcium phosphatomalonate showed two breaks in the vicinity of 1:1 and 1:2 mole ratios. The two breaks, thus evidenced the formation of two complexes 1:1 and 1:2. The curve for calcium phosphatosuccinate showed three breaks in the vicinity of 1:1, 1:2 and 1:3 mole ratio respectively, between calcium phosphate and succinic acid. The three breaks, thus evidenced the formation of three complexes 1:1, 1:2 and 1:3 between calcium phosphate and succinic acid.

The curve for calcium phosphatoglutarate showed three breaks in the vicinity of 1:1, 1:2 and 1:3 mole ratio respectively showing the evidence for the formation of three complexes.

In each case complete dissolution of the original suspension of calcium phosphate took place beyond the third break point. This suggests that the complexes are moderately soluble; however, they are much more soluble than calcium phosphate.

In all the titrations, specific conductivity continued to increase with the addition of titrant, at the break points; however, the rate of increase of specific conductivities decreased. The volume of titrant in all the cases was so adjusted that there could not possibly be any dilution effect. In case of all the titrations carried out, the initially taken suspensions ultimately went into solution. Upon titration, indicating non-replacement type of chemical interactions between the reactants, a complete replacement reaction under the experimental conditions would have resulted in precipitation of the calcium salt of the titrant acid.

The elemental analyses of the solid compounds isolated were found to be in close agreement with the values required for a 1:2 complex between both calcium phosphatomalonic acid and calcium phosphatosuccinic acid. The corresponding complex with glutaric acid could not be isolated.

The melting/decomposition temperature of the compounds isolated in case of malonic and succinic acids (Table-1) suggests them to be genuine compounds and not stoichiometric mixtures of the reactants. Presence of phosphate in the

complexes has been confirmed by ammonium molybdate test. The yellow precipitation of ammonium phosphomolybdate, however, is considerably delayed. This might be due to the presence of phosphate in the complexes in a high state of association.

Formation of the complexes seems to be due to the partial protonation of the phosphate anions of calcium phosphate in stages, by the dibasic acids. Calcium ions seem to be bridging the partially protonated phosphate and the dibasic acid anion complexes are probably of the mixed acid-salt type, *i.e.*, mixed complexes of calcium with phosphoric and dibasic acids.

The 1:3 complexes, however, might be formed by the association of the 1:2 complexes with a third molecule of the dibasic acid, probably through the intermolecular hydrogen bonding, or by the adsorption of a third dibasic acid molecule by the 1:2 complex. Further partial protonation of phosphate ions beyond the formation of 1:2 complex is not possible.

TABLE-2
CONDUCTOMETRIC TITRATIONS

Initial value = 100 mL

Complex (g)	Titrant	Inflection point (mL) Found (Calcd.)		
		1:1	1:2	1:3
Calcium phosphate (0.031)	0.5 M Malonic acid	0.205 (0.200)	0.420 (0.400)	— —
Calcium Phosphate (0.031)	0.5 M Succinic acid	0.205 (0.200)	0.415 (0.400)	0.625 (0.600)
Calcium phosphate (0.031)	0.5 M Glutaric acid	0.225 (0.200)	0.400 (0.400)	0.655 (0.600)

REFERENCE

A.K. Banerjee, T.V.R.K. Rao and S.K. Roy, *J. Indian Chem. Soc.*, **63**, 460 (1986).

(Received: 24 September 1996; Accepted: 3 February 1997)

AJC-1242