

Influence of Weak Acids on Sparingly Soluble Phosphates

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From a systematic study of the solubility of the phosphates of Ba, Sr, Cr, Zn, Mn, Co, Cu, Bi, Cd, Pb, Al, and Mg in solutions of some organic acids, the solubility can be arranged in the order: oxalic > tartaric > citric > formic > acetic. The P_2O_5 -solubility gradually increases with the increase in the concentration of carbonic acid in the case of Mg, Ba, Sr, Mn, Co, Cu, and Bi phosphates, but it decreases in the case of Al, Cr, Cd, Pb, and Zn phosphates. In glycine, unlike other acids, copper phosphate instead of magnesium phosphate shows the maximum solubility. Solubility behaviour of these phosphates has been explained on the basis of pH of the equilibrium mixtures, dissociation constants, and possible reactions of the acids.

Various workers¹⁻³ have studied the solubility of mineral phosphates in citric acid. Cremona⁴ studied the solubility of natural phosphates and slag in various organic and dilute mineral acids. Calcagni⁵ studied the action of SO_2 on natural phosphates. Lehr and Wesemael⁶ and Dhar and Sharma⁷ studied the influence of salts on the solubility of phosphates. Copaux and Darie⁸ made a comparative study of the solubility of various natural phosphates by potentiometer. The present investigation deals with the influence of oxalic, citric, tartaric, formic, acetic, carbonic, and amino-acetic acids on the phosphates of Ba, Sr, Cr, Zn, Mn, Co, Cu, Bi, Cd, Pb, Al, and Mg regarding which practically no comparative work appears in the literature.

EXPERIMENTAL

$AlPO_4 \cdot H_2O$, $CrPO_4 \cdot 6H_2O$, $BaHPO_4 \cdot 2H_2O$, $SrHPO_4$, $MgHPO_4 \cdot 3H_2O$, $Zn_3(PO_4)_2 \cdot 4H_2O$, $MnHPO_4 \cdot 3H_2O$, $Co_3(PO_4)_2$, $Cu_3(PO_4)_2 \cdot 3H_2O$, $BiPO_4$, $Cd_3(PO_4)_2$, and $Pb_3(PO_4)_2$ used were pure laboratory chemicals. Each sample used was first analysed for its P_2O_5 content and the percentage of P_2O_5 corresponded to the above mentioned formulas. The organic acids used were of chemically pure quality and their concentrations employed were 0.1N, 0.02N, 0.01N, and 0.001N. Carbonic acid of different concentrations was prepared by passing CO_2 gas (prepared by the action of HCl on marble pieces) for different periods in double distilled water. The concentration of CO_2 was computed by titrating⁹ against a standard baryta solution.

1. Robertson, *J. Soc. Chem. Ind.* 1916, 35, 217.
2. Tocher, *J. Agric. Sci.*, 1922, 12, 125.
3. Maurice and Martens, *Chem. Abs.*, 1938, 32, 5141.
4. *Ann. chim. Appl.*, 1917, 7, 200.
5. *Ibid.*, 1930, 20, 74.
6. *J. Soil Sci.*, 1952, 3, 125.
7. *Proc. Natl. Acad. Sci.*, 1956, 25A, 515, 596.
8. *Bull. soc. chim.*, 1924, 35, 1115.
9. Vogel, "Quantitative Inorganic Analysis", 2nd ed., Longmans, 1960, p. 242.

TABLE I

Solubility of the phosphates in various acids.

Phos- phates,	Oxalic (pH 1.7).		Tartaric (pH 2.2).		Citric (pH 2.2).		Formic (pH 2.3).		Acetic (pH 2.5).		Carbonic.		0.2N Glycine ³ in. (pH 6.58).	
	**P ₂ O ₅	pH.	**P ₂ O ₅	pH.	P ₂ O ₅	pH.	P ₂ O ₅	pH.	P ₂ O ₅	pH.	P ₂ O ₅	pH.	P ₂ O ₅	pH.
Al	0.0617	3.28	1.2414	3.16	0.7906	3.04	0.3212	3.22	0.2324	4.12	0.0445	6.58	0.1297	6.96
Cr	0.0509	2.52	0.4262	3.24	0.3768	3.56	0.2904	3.36	0.2224	4.32	0.0271	6.72	0.1266	7.14
Ba	0.0432	2.6690	2.32	3.12	2.1301	3.26	2.0441	3.30	1.0808	3.98	0.1074	6.22	0.2007	6.88
Sr	0.1071	3.0480	2.46	3.70	2.7060	4.06	2.0760	3.88	1.4072	4.84	0.2656	6.88	0.4910	7.88
Mg	0.2347	4.9260	2.80	3.70	4.1560	3.86	3.8000	3.80	3.1000	4.64	0.4226	6.62	0.5281	7.46
Zn	0.0162	3.4180	3.54	3.40	2.2980	3.54	1.7722	3.58	0.5536	4.24	Insoluble	6.52	0.2532	7.44
Mn	0.0165	3.9540	3.28	3.88	3.0341	4.22	2.8780	3.92	1.6306	4.36	0.0687	6.32	0.1421	7.32
Co	0.0189	4.1360	2.86	3.78	3.8160	3.90	3.4000	3.98	2.1446	4.60	0.1674	6.50	0.4972	6.74
Cu	0.0579	3.2060	2.90	3.0820	2.8300	3.14	1.0216	3.38	0.7474	4.10	0.0821	6.56	1.6980	4.44
Bi	0.0182	1.2320	2.06	0.2904	0.2656	2.48	0.1852	2.58	0.1720	3.26	0.0210	5.08	0.1329	6.32
Cd	0.0123	2.4770	2.40	1.1682	1.1242	3.06	0.9078	3.30	0.3800	4.24	0.0086	6.46	0.1359	6.82
Pb	0.0635	2.3660	2.00	0.3898	0.3274	2.58	0.3101	2.00	0.3044	3.28	0.0333	4.88	0.2564	5.16

* Soln. containing 375.3 ml CO₂ per litre at N.T.P.; pH 4.48.** P₂O₅ conc. expressed in g./litre.

‡ pH refers to filtrate.

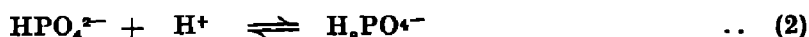
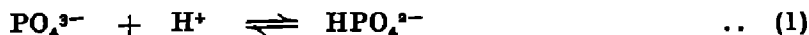
The phosphate sample (1g.) was shaken with the solution (100ml) for 5 min. in a 250-ml Jena glass bottle and the contents were allowed to stand for 24 hr. in a "Gallenkamp" thermostat, maintained at $25^{\circ} \pm 0.1^{\circ}$. On the next day, the clear liquid was filtered. Aliquot portions were taken for the estimation of P_2O_5 volumetrically¹⁰, using ammonium molybdate. The pH of the solution was also determined as in our previous communication¹¹. The experiments were carried out under similar conditions and with as much uniformity as possible so as to minimise the error in solubility due to variation in the time of contact of the phosphate and the solution. Observations in large number were taken. Some of the typical results are summarised in Table I.

DISCUSSION

Solubility of Phosphates in Water, Oxalic, Tartaric, Citric, Formic, and Acetic Acids.—From Table I, it is evident that the solubility in water of the phosphates of metals lies in the order: $Mg > Sr > Pb > Al > Cu > Cr > Ba > Co > Bi > Mn > Zn > Cd$.

The solubility of the phosphates in these acids can be arranged in the following decreasing order: oxalic > tartaric > citric > formic > acetic.

Solubilising action of these acids on the sparingly soluble phosphates can be explained on the basis of their dissociation constants¹². The H^+ ions available from the acids have a dissolving action on the sparingly soluble phosphates; hence PO_4^{3-} ions available from the sparingly soluble phosphates are converted to less dissociated HPO_4^{2-} and $H_2PO_4^-$ ions according to equations (1) and (2):



pH of the equilibrium mixture also supports this contention. In case of bismuth and lead phosphates, the final pH values at all dilutions of the acids are found to be comparatively low with respect to the corresponding pH values in other phosphates. This may be either due to the smaller amount of the metallic ions going into the solution or due to the adsorption of basic ions on the solid residue of the phosphate.

The results indicate that anions are also involved and the solubility of the phosphates becomes greater in the case of that acid in which the anion complex with the metal of the phosphate is more soluble, irrespective of the pH of the equilibrium mixture. The solubility of aluminium phosphate in 0.1N solutions of tartaric and citric acids supports this view.

Solubility of the Phosphates in Carbonic Acid.—The results indicate that the P_2O_5 -solubility gradually increases with the increase in the concentration of carbonic acid in the case of phosphates of Mg, Ba, Sr, Mn, Co, Cu, and Bi (magnesium phosphate being the most soluble). In the case of phosphates of Al, Cr, Cd, Pb, and Zn, the P_2O_5 -solubility decreases

10. Vogel, *ibid.*, p. 380.

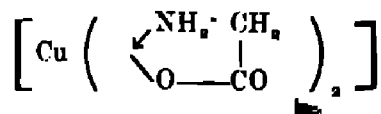
11. Joshi and Jain, *this Journal*, 1964, 41, 33.

12. Hodgeman, "Hand Book of Physics and Chemistry", pp. 1466-77 and 1504-7.

in presence of carbonic acid, so much so, that zinc phosphate is practically insoluble in it. Likewise, the dissolving power of carbonic acid can be explained on the basis of dissociation constants.

Solubility of the Phosphates in Glycine.—In glycine solutions, the phosphates are more soluble than in water alone.

Unlike other acids, copper phosphate, instead of magnesium phosphate, showed maximum solubility in glycine. Of particular interest is the fact that at the same dilution of 0.1*N*, copper phosphate is more soluble in glycine than in acetic acid. In this particular case, *pH* of the solution does not seem to have any relation with the solubility of the phosphate. With other phosphates, however, the solubility increases with the decrease of *pH* value. In the case of copper phosphate, the supernatant liquid is deep blue in colour and the marked increase in solubility can be explained due to formation of the deep blue copper-glycine complex in solution.



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