

A STUDY ON PYROPHOSPHATO COMPLEXES WITH FERTILIZER TRACE ELEMENTS

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Abstract— To evaluate the capability of pyrophosphate ion as a carrier of fertilizer trace elements, pyrophosphato complexes with manganous, cupric, ferrous and zinc ions were studied by spectrophotometry and polarography.

The soluble complexes of Mn^{2+} , Cu^{2+} , Fe^{2+} and Zn^{2+} with pyrophosphate ion appeared to be $[Mn(H_xP_2O_7)_2]^{(6-2x)}$, $[Cu(H_xP_2O_7)_2]^{(6-2x)}$, $[Fe(H_xP_2O_7)_2]^{(6-2x)}$ and $[Zn(H_xP_2O_7)_2]^{(2-x)}$, and the logarithmic values of their stability constants were measured to be 1.79, 3.45, 5.08 and 6.43 at pH 10, respectively.

However, by adding excess corresponding metal ion, the soluble pyrophosphato complexes were ultimately changed to amorphous precipitates.

INTRODUCTION

The availability of metallic fertilizer trace elements (FTE) would be diminished by being incorporated to either conventional phosphatic or high analysis fertilizer, forming almost insoluble orthophosphates [1-3]. In application to fertilizer, therefore, it is important to redissolve the FTE-orthophosphates in water or to make FTE into stable and soluble complexes at preparing stage. It is well known that a number of complexing agents including polyphosphates exhibit solubilizing effect on some sparingly soluble salts [4,5]. In general, polyphosphates have been most widely used as industrial water-treating agents [6], fertilizers [7-11], dispersants [12] and corrosion inhibitors [13,14].

Numbers of polyphosphate systems have been investigated including metal complexes of polyphosphates have been reported [15-18], while few reports [19,20] about the complex formation of polyphosphates with FTE are presently available.

In this study, the pyrophosphato complexes with Mn^{2+} , Cu^{2+} , Fe^{2+} and Zn^{2+} were identified and the related chemical formulae as well as individual stability constants were provided.

EXPERIMENTAL

Chemicals

All chemicals used in this experiment were E.P. grade except FTE-orthophosphates which were

prepared in our laboratory, $Na_3PO_4 \cdot 12H_2O$ and $Na_4P_2O_7 \cdot 10H_2O$ were used for the sources of orthophosphate and pyrophosphate ions, respectively. Manganous, cupric, ferrous and zinc orthophosphates were prepared by reaction of each sulfate of the FTE with stoichiometric amount of sodium orthophosphate in aqueous solution, and resulting precipitates were filtered, washed and dried at 110°C.

Light transmittance measurement of $MSO_4 \cdot Na_4P_2O_7 \cdot H_2O$ system

To ascertain the $M^{2+}/P_2O_7^{4-}$ molar ratio of soluble complexes and precipitates between M^{2+} (divalent FTE-ion) and pyrophosphate ion, the light transmittances of $MSO_4 \cdot Na_4P_2O_7 \cdot H_2O$ systems were measured using spectrophotometer (Bausch & Lomb Spectronic 20).

Mixtures having various $M^{2+}/P_2O_7^{4-}$ molar ratios were prepared by dissolving different proportions of FTE-sulfate and sodium pyrophosphate in distilled water. The concentrations of sodium pyrophosphate in $MnSO_4 \cdot Na_4P_2O_7 \cdot H_2O$, $CuSO_4 \cdot Na_4P_2O_7 \cdot H_2O$, $FeSO_4 \cdot Na_4P_2O_7 \cdot H_2O$ and $ZnSO_4 \cdot Na_4P_2O_7 \cdot H_2O$ systems were selected to 1.8×10^{-3} , 1.0×10^{-3} , 6.0×10^{-4} and 1.2×10^{-3} mole/l, respectively.

Applied wave lengths for the above systems were 400, 540, 533 and 400nm, respectively. And it was observed that light of the wave lengths was not absorbed by complex in the corresponding system.

Polarographic analysis

Polarographic analysis was performed to evaluate the chemical formulae and stability constants of the pyrophosphato complexes formed in the systems mentioned previously.

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The concentration of all the divalent FTE-ions was selected to 6.25×10^{-5} mole/l. The solutions having various $M^{2+}/P_2O_7^{4-}$ molar ratios were made by adding varied amounts of sodium pyrophosphate to each FTE-sulfate solution. The pH's of the solutions were controlled to 10 with $NaHCO_3$ - $NaOH$ buffer solution.

The half-wave potentials respect to the divalent FTE-ions in the prepared systems were measured using a polarograph (EG & G Princeton Applied Research Model 264). Selected supporting electrolyte was $2.5 \times 10^{-2} M$ - KNO_3 .

RESULTS AND DISCUSSION

Although results were not arranged in this paper, a solubilizing effect of the sodium pyrophosphate on almost insoluble FTE-orthophosphates, due to the formation of soluble complexes between pyrophosphate ion and cation of each orthophosphate, was confirmed in this experiment.

Aoki et al. [21] measured light transmittances of Mn^{2+} - NH_4^+ - $H_4P_2O_7$ - H_2O system having various $Mn^{2+}/P_2O_7^{4-}$ molar ratios to confirm a chemical formula of pyrophosphato complex with manganous ion, and reported the chemical formula of complex to be $[Mn(P_2O_7)_2]^{6-}$.

In this study, light transmittance measurement and polarographic analysis of MSO_4 - $Na_4P_2O_7$ - H_2O systems varying $M^{2+}/P_2O_7^{4-}$ molar ratios were performed for analogous purpose.

The light transmittances of $MnSO_4$ - $Na_4P_2O_7$ - H_2O and $CuSO_4$ - $Na_4P_2O_7$ - H_2O systems against $M^{2+}/P_2O_7^{4-}$ molar ratios were plotted in Figs. 1-2. Since the light absorbing entity, for the wave lengths applied in this experiment, is colloidal suspension of precipitate and

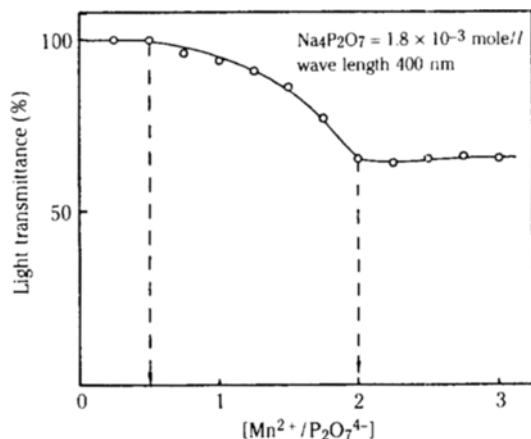


Fig. 1. Plot of light transmittance vs. $Mn^{2+}/P_2O_7^{4-}$ molar ratio in the $MnSO_4$ - $Na_4P_2O_7$ - H_2O system.

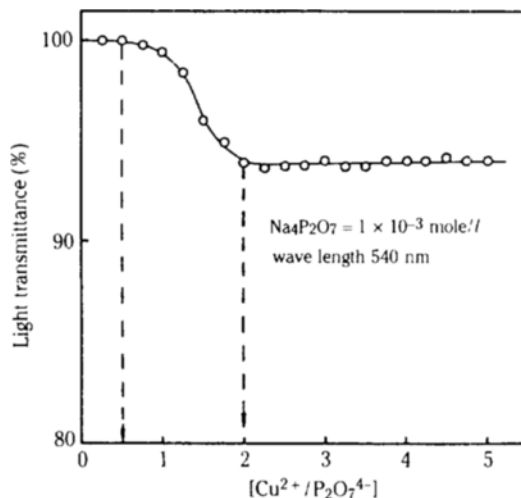


Fig. 2. Plot of light transmittance vs. $Cu^{2+}/P_2O_7^{4-}$ molar ratio in the $CuSO_4$ - $Na_4P_2O_7$ - H_2O system.

the region of lower $M^{2+}/P_2O_7^{4-}$ molar ratio than 0.5 maintains 100 percent light transmittance, soluble complex is dominant in the region. Hence, it is reasonable [21] to consider the $M^{2+}/P_2O_7^{4-}$ molar ratio of soluble complexes between either manganous or cupric ion and pyrophosphate ion as 0.5. Considering the pyrophosphate ions are present as $[H_2P_2O_7]^{4-}$ in aqueous solutions by hydrolysis, it appears that chemical formulae of the pyrophosphato complexes formed with manganous or cupric ions are $[Mn(H_2P_2O_7)_2]^{6-}$ and $[Cu(H_2P_2O_7)_2]^{6-}$, respectively. By further adding manganous or cupric ion, the soluble complexes are ultimately changed to colloidal precipitates. This is proved from results that the light transmittances of solutions having $M^{2+}/P_2O_7^{4-}$ molar ratio between 0.5 and 2 are decreased continuously with increasing the molar ratio. Also the light transmittances show nearly constant values in the region where the $M^{2+}/P_2O_7^{4-}$ molar ratio is 2 and above, indicating that there is no further precipitation in the region because the remaining soluble pyrophosphato complexes are completely changed to precipitates at about 2 of the molar ratio. Therefore, it is believed that $M^{2+}/P_2O_7^{4-}$ molar ratio of the amorphous precipitates formed in these systems is 2.

Greenfield et al. [22] have reported that pyrophosphates precipitated from the solutions of soluble metal salts with sodium pyrophosphate are amorphous and they exist for long time without becoming crystalline.

Fig. 3 is a plot of light transmittances versus molar ratios of ferrous ion to pyrophosphate ion in $FeSO_4$ - $Na_4P_2O_7$ - H_2O system.

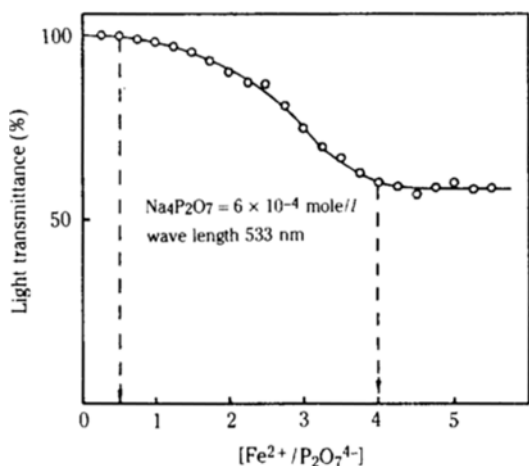


Fig. 3. Plot of light transmittance vs. $Fe^{2+}/P_2O_7^{4-}$ molar ratio in the $FeSO_4-Na_4P_2O_7-H_2O$ system.

The light transmittances, as those of $MnSO_4-Na_4P_2O_7-H_2O$ and $CuSO_4-Na_4P_2O_7-H_2O$ systems, are 100 percent in the region of $Fe^{2+}/P_2O_7^{4-}$ molar ratio 0.5 and less, and it seems that the soluble complex formed between ferrous ion and pyrophosphate ion is $[Fe(H_xP_2O_7)_2]^{(6-2x)}$. Similarly, the $Fe^{2+}/P_2O_7^{4-}$ molar ratio of precipitate seems to be 4 because the light transmittances remain almost constant at the $Fe^{2+}/P_2O_7^{4-}$ molar ratio of 4 and above.

Fig. 4 shows the relationship between light transmittance and $Zn^{2+}/P_2O_7^{4-}$ molar ratio in $ZnSO_4-Na_4P_2O_7-H_2O$ system. By similar consideration, we can predict that the chemical formula of soluble pyrophosphato complex is $[ZnH_xP_2O_7]^{(2-x)}$ and that the $Zn^{2+}/P_2O_7^{4-}$ molar ratio of precipitate is 2 from these plots.

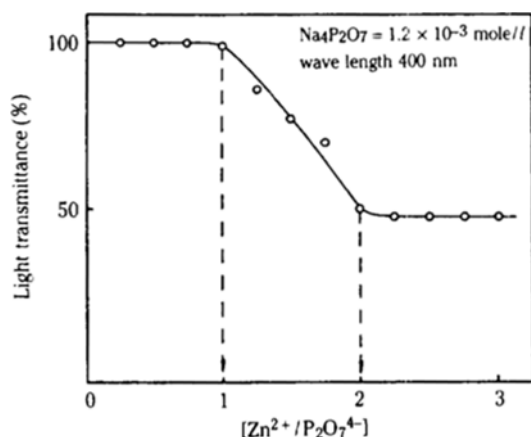


Fig. 4. Plot of light transmittance vs. $Zn^{2+}/P_2O_7^{4-}$ molar ratio in the $ZnSO_4-Na_4P_2O_7-H_2O$ system.

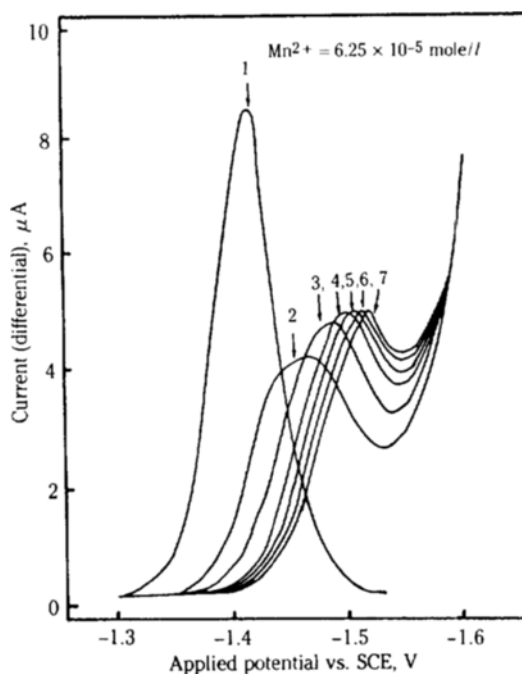


Fig. 5. Effect of sodium pyrophosphate concentration on the differential pulse polarographic wave of manganous ion in the supporting electrolyte of 2.5×10^{-2} M- KNO_3 solution. concentration of sodium pyrophosphate (mole/l): 0 (1), 3.75×10^{-5} (2), 6.25×10^{-5} (3), 10.00×10^{-5} (4), 12.50×10^{-5} (5), 16.25×10^{-5} (6), 18.75×10^{-5} (7).

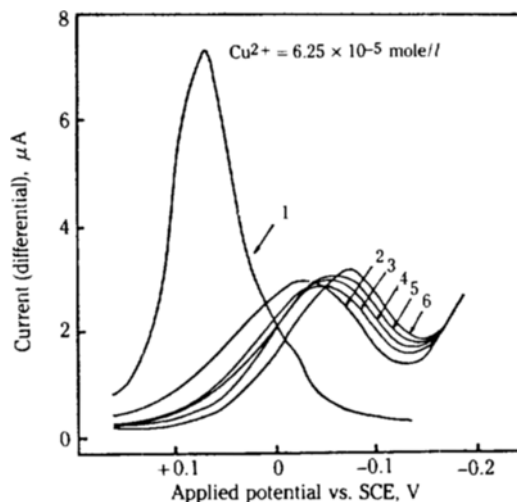


Fig. 6. Effect of sodium pyrophosphate concentration on the differential pulse polarographic wave of cupric ion in the supporting electrolyte of 2.5×10^{-2} M- KNO_3 solution. concentration of sodium pyrophosphate (mole/l): 0 (1), 6.25×10^{-5} (2), 10.00×10^{-5} (3), 12.50×10^{-5} (4), 16.25×10^{-5} (5), 18.75×10^{-5} (6).

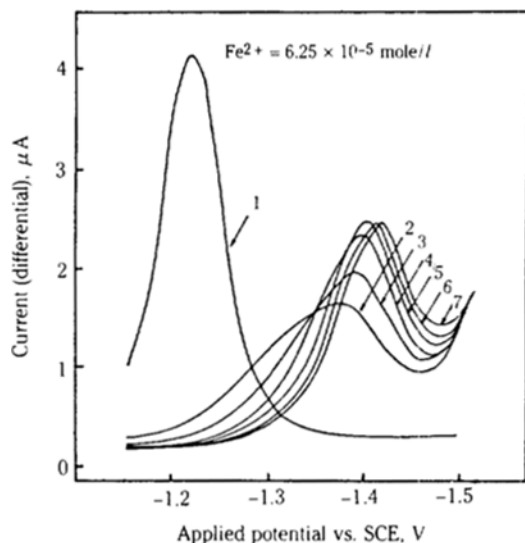


Fig. 7. Effect of sodium pyrophosphate concentration on the differential pulse polarographic wave of ferrous ion in the supporting electrolyte of 2.5×10^{-2} M-KNO₃ solution.

concentration of sodium pyrophosphate (mole/l): 0 (1), 3.75×10^{-5} (2), 6.25×10^{-5} (3), 10.00×10^{-5} (4), 12.50×10^{-5} (5), 16.25×10^{-5} (6), 18.75×10^{-5} (7).

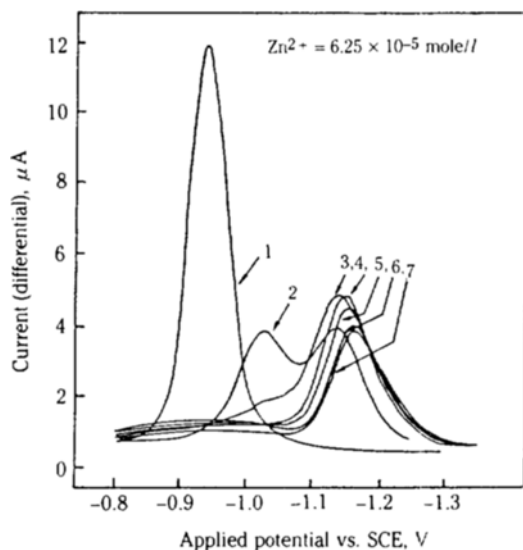


Fig. 8. Effect of sodium pyrophosphate concentration on the differential pulse polarographic wave of zinc ion in the supporting electrolyte of 2.5×10^{-2} M-KNO₃ solution.

concentration of sodium pyrophosphate (mole/l): 0 (1), 3.75×10^{-5} (2), 6.25×10^{-5} (3), 10.00×10^{-5} (4), 12.50×10^{-5} (5), 16.25×10^{-5} (6), 18.75×10^{-5} (7).

Stability constant of complexes can be evaluated by several methods such as titration method [23], spectrophotometry [24] and polarography [25]. In this study, the stability constants of pyrophosphato complexes formed with each FTE-ion were evaluated by polarography.

The differential pulse polarographic waves of metal or complex ion, the potential of maximum current of the waves corresponds to the half-wave potential [26], are given in Figs. 5-8. The half-wave potentials obtained from these polarographic waves are listed in Table 1. As can be seen from Figs. 5-8 and Table 1, addition of sodium pyrophosphate caused the half-wave potentials of metal ions to shift to more negative values.

Lingane [27] has suggested a relationship between the shift of half-wave potential ($\Delta E_{1/2}$) and the ligand concentration (C_L) by the following equation.

$$\Delta E_{1/2} = -\frac{0.0591}{n} \log K - \frac{0.0591r}{n} \log C_L$$

where n is the valence of metal ion, K is the stability constant of complex, and r is the molar ratio of pyrophosphate ion to metal ion in complex. The plot of $\Delta E_{1/2}$ against $\log C_L$ from the data in Table 1 is shown in Fig. 9, and linear relationship between them are established. From the slopes of these lines, the $P_2O_7^{4-}/M^{2+}$ molar ratios of Mn^{2+} , Cu^{2+} , Fe^{2+} and Zn^{2+} complexes with pyrophosphate ligand were deduced to be 2.03, 2.06, 1.96 and 1.12, indicating that the formulae

Table 1. Half-wave potential of cations in the various concentrations of aqueous pyrophosphate solution. Used supporting electrolyte is 2.5×10^{-2} M-KNO₃

cation	$C_L \times 10^5$	$E_{1/2}$	cation	$C_L \times 10^5$	$E_{1/2}$
Mn^{2+}	0	-1.414	Fe^{2+}	0	-1.216
	3.75	-1.462		3.75	-1.372
	6.25	-1.486		6.25	-1.384
	10.00	-1.498		10.00	-1.396
	12.50	-1.504		12.50	-1.399
	16.25	-1.510		16.25	-1.405
	18.75	-1.516		18.75	-1.411
Cu^{2+}	0	+0.084	Zn^{2+}	0	-0.994
	6.25	-0.034		3.75	-1.139
	10.00	-0.052		6.25	-1.142
	12.50	-0.055		10.00	-1.154
	16.25	-0.058		12.50	-1.160
	18.75	-0.070		16.25	-1.163
				18.75	-1.166

C_L : concentration of pyrophosphate ion ligand (mole/l)
 $E_{1/2}$: half-wave potential

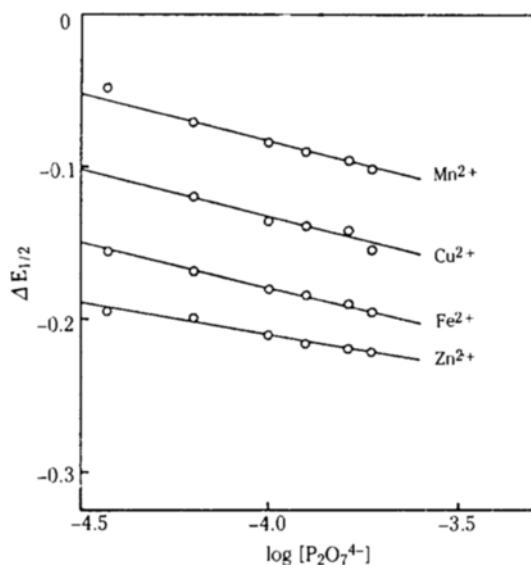


Fig. 9. Plot of $\Delta E_{1/2}$ vs. $\log [P_2O_7^{4-}]$.

Table 2. Stability constant and $P_2O_7^{4-}/M^{2+}$ molar ratio of pyrophosphato complexes

cation of the complex	intercept	logK	slope	molar ratio ($P_2O_7^{4-}/M^{2+}$)
Mn ²⁺	-0.053	1.79	-0.060	2.03
Cu ²⁺	-0.102	3.45	-0.061	2.06
Fe ²⁺	-0.150	5.08	-0.058	1.96
Zn ²⁺	-0.190	6.43	-0.033	1.12

of the most prevalent pyrophosphato complexes in the systems were $[Mn(H_xP_2O_7)_2]^{(6-2x)-}$, $[Cu(H_xP_2O_7)_2]^{(6-2x)-}$, $[Fe(H_xP_2O_7)_2]^{(6-2x)-}$ and $[ZnH_xP_2O_7]^{(2-x)-}$. These results match well with the findings from Figs. 1-4.

The logarithmic stability constants of the pyrophosphato complexes can be calculated from the intercepts of Fig. 9 and obtained the following sequence of values in parentheses; $Mn^{2+}(1.79) < Cu^{2+}(3.45) < Fe^{2+}(5.08) < Zn^{2+}(6.43)$. These results were summarized in Table 2.

CONCLUSIONS

1. Chemical formulae of soluble pyrophosphato complexes formed with manganese cupric, ferrous and zinc ion appeared to be $[Mn(H_xP_2O_7)_2]^{(6-2x)-}$, $[Cu(H_xP_2O_7)_2]^{(6-2x)-}$, $[Fe(H_xP_2O_7)_2]^{(6-2x)-}$ and $[ZnH_xP_2O_7]^{(2-x)-}$, and the logarithmic values of their stability constants were 1.79, 3.45, 5.08 and 6.43 at pH 10, respectively.

2. The soluble pyrophosphato complexes with FTE's were changed to amorphous precipitates by ad-

ding excess corresponding FTE-ion. And $M^{2+}/P_2O_7^{4-}$ molar ratios of the precipitates formed in $MnSO_4-Na_4P_2O_7-H_2O$, $CuSO_4-Na_4P_2O_7-H_2O$ and $ZnSO_4-Na_4P_2O_7-H_2O$ systems were 2, respectively, whereas the ratio in $FeSO_4-Na_4P_2O_7-H_2O$ system was 4.

NOMENCLATURE

- C_L : concentration of pyrophosphate ion ligand (mole/l)
 $\Delta E_{1/2}$: difference in half-wave potential between simple metal ion and complex (volt)
 K : stability constant of complex
 n : valence of metal ion
 r : molar ratio of pyrophosphate ion/metal ion in complex

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