Potentiometric measurement of stability constants of complexes between fulvic acid carboxylate and Fe^{3+}

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Abstract

The stability constants of complexes formed between iron (III) and fulvic acid extracted from organic manures and wastes such as urban domestic sewage sludge, farmyard manure, poultry manure and sulfitation pressmud were investigated by the potentiometric titration method in an ionic medium of 0.1 M KNO_3 at 25±1 °C. A modification of the Katchalsky's model was employed for the estimation of stability constants. The displacement of the titration curves due to presence of Fe^{3+} in FA solutions formed the basis of calculations. The weak acidic property of fulvic acids due to carboxyl groups resulted in buffering over a wide range of pH; fulvic acids were completely neutralized in the pH range of 7.00–8.85. Apparent dissociation constants (pK_{APP}) of weakly acidic carboxyl groups were a direct function of degree of dissociation (α_L) in the mid-range of titration curves but were non-linear at high and low α_L values. The stability constants for formation of Fe–FA complexes (log β_{Fe}) calculated from the titration data were in the range of 5.64–7.55, depending upon α_L and electrostatic properties of fulvic acids. The relatively high stability constants of Fe–FA complexes in comparison to those with other competing cations suggest that the Fe–FA complexes are relatively stable in a soil environment.

Introduction

The aqueous solutions of fulvic acids (FA) form complexes of varying thermodynamic stability with transitional metal cations. The ubiquitous presence of soil organic matter in the soil solution is considered to be instrumental in supplying trace and heavy metals such as Fe to plants grown in soils with neutral and alkaline pH. The complexation of Fe by fulvic acid protects it from precipitation and renders it available to plants (Hodgson, 1963; Pandeya and Singh, 1997; Singh and Sinha, 1977). The stability constant of humic matter–metal complex is one of the parameters determining the thermodynamic stability of the metal complexes and, thus, their effectiveness in augmenting or decreasing the availability of metal cations to plants. Procedures for determining stability constants of complexes formed between metal cations and organic acids as described in literature (Bjerum, 1941; Hartley et al., 1970; Rosotti and Rosotti, 1961; Tanford, 1961; Van Holde, 1971) have been used extensively for elucidation of complexation reactions between fulvic acids and metal cations (Gregor et al.,

1955, 1989; Gregor and Powell, 1986; Khanna and Stevenson, 1962; Pandeya, 1993; Pandeya and Singh, 1997; Schnitzer and Hansen, 1970; Sposito et al., 1978; Sudersanan and Sundaram, 1986; Wilson and Kinney, 1977; Young et al., 1982; Zunio et al., 1982). Most of the experimental results in the literature, however, are limited to the studies on stability constants of bivalent metal cation–fulvic acids complexes with limited studies on stability constant of the formation of Fe^{3+}–FA complexes (Langford and Khan, 1975; Pandeya, 1993; Pandeya and Singh, 1997; Stevenson, 1982). This is probably due to the fact that the assumptions underlying the principles of determination of stability constants are not met in experimental conditions involving Fe (III). Potentiometric measurement of stability constants of Fe^{3+}–FA complexes holds promise but no serious attempt has so far been made to elucidate the principles underlying the methodology. As such, there is evident lack of data on stability constants of Fe^{3+}–FA complexes in literature.

The present paper reports the stability constants of fulvic acid carboxylate–Fe (III) complexes, as determined by the potentiometric titration method. The fulvic

acids were extracted from various organic sources, and differed in terms of degree and nature of acidity, clustering of charges due to different molecular size and shape, and change in configuration due to change in pH of the medium.

Theoretical considerations

Simultaneous competitive equilibria of metal cations and protons for a complexing ligand have been used as the basis of determining stability constants of metal complexes. The mathematical model of Katchalsky, which has been critically documented by Tanford (1961) and subsequently employed by Young et al. (1981) for describing the potentiometric behaviour of polyelectrolytes, has been used in this paper as the basis of the development of a model for determination of stability constants of FA carboxylate Fe^{3+} complexes.

Potentiometric titration of FA in absence of metal

The dissociation of –COOH in fulvic acid on titration with an alkali may be expressed as:

$$LH = L^- + H^+ \tag{1}$$

Where LH is undissociated COOH ligand, L^- is dissociated ligand, and H^+ is proton, for which the ionization constant may be written as:

$$K = (L^-(H^+))/(LH) \tag{2}$$

This constant, on rearrangement, assumes the form:

$$pK = pH - \log(L^-) + \log(LH) \tag{3}$$

The dissociation of the carboxyl groups of fulvic acids extends over a wide range of pH. This indicates that –COOH group of fulvic acids are not present in such a steric disposition as to undergo simultaneous dissociation during titration with alkali. The buffering zone during dissociation of this functional group which extends over a wide pH range is attributed to the configurational changes of fulvic acids on the expansion of macromolecules with an increase in pH of the titration medium (Sposito and Holtzclaw, 1977). The considerations needed to characterize their dissociation behaviour are (Pandeya, 1992; Young et al., 1981):

Polymeric charge density

Titration of fulvic acids with a base leads to a gradual increase in the number of dissociated functional groups per macromolcule of fulvic acid. The build-up of negative charge on the polymeric fulvic acid on its titration with an alkali may restrict further dissociation of the acidic functional groups. Consequently, the values of dissociation constants of the acidic functional groups will decrease on increase of the pH of the medium (Tanford, 1961). Electrostatic restrictions on dissociation of the functional group, therefore, need to be considered in elucidation of patterns of dissociation of –COOH in FA.

Polymeric radius and configurational changes

Titration of fulvic acids with a base leads to the opening of its coiled structure (Sposito and Holtzclaw, 1977). This may change the polymeric charge density and spatial disposition of functional groups in aqueous systems which ultimately may influence the dissociation pattern of ligands.

Taking into consideration the points in 'Polymeric charge density' and 'Polymeric radius and configurational changes' above, following equations documented by Tanford (1961) were used for describing the dissociation pattern of –COOH and variations in pK due to a degree of dissociation.

$$pK_{APP} = pK_{INT} + 0.868\, nW\, \alpha_L \tag{4}$$

Where pK_{APP} is the apparent pK at any specific degree of dissociation and is equal to:

$$pK_{APP} = -\log[\{\alpha_L/(1-\alpha_L)\}H^+] \tag{5}$$

α_L is degree of dissociation which is equal to

$$(L^-)/(T) \tag{6}$$

where L^- is dissociated ligand concentration and T is total carboxyl group concentration, and pK_{INT} is intrinsic pK at zero degree of dissociation, n is number of functional groups per molecule of FA, and W is an electrostatic function.

The dissociated ligand concentration may be calculated from the titration data by equation

$$L^- = (KOH) + (H^+) - (OH^-) \tag{7}$$

where (KOH) is the amount of alkali added (meq) in FA solution and H^+ and OH^- are the hydrogen and hydroxyl ion concentrations.

A plot of the titration data according to Equation (4) should yield a straight line with intercept equal to pK_{INT} and the slope equal to $0.868 nW$.

Potentiometric titration of FA in presence of Fe^{3+}

The potentiometric titration of an acidic polycarboxylate like FA in the presence of Fe^{3+} will obey the following relationship:

$$T = L^- + LH + \Sigma x(FeL_x^{3-x}) \tag{8}$$

Where T is concentration of –COOH groups, and x is an integral number, FeL_x is Fe^{3+}-ligand complex and the sum should be over all x,

$$LH = T - (KOH) - H^+ \tag{9}$$

$$(L^-) = [(LH)K_{APP}]/(H^+) \tag{10}$$

Since pK_{APP} is a function of α_L (Equation (4)), values of L^- in Equation (10) cannot be evaluated directly in presence of a metal cation. Equation (10), therefore, needs to be solved by iteration. The estimates of $\Sigma x(FeL_x^{3-x})$ can be made from Equation (8) by using calculated values of L^- from Equation (10) and estimated values of LH and T from the potentiometric titration data.

Bjerrum formation function $\tilde{n}$, which is defined as the average number of ligands bonded to each metal cation can be derived from the equation:

$$\tilde{n} = \Sigma x(Fe_{Lx}^{3-x})/Fe_t^{3+} \tag{11}$$

where Fe_t^{3+} is total metal cation present in FA solution.

It is assumed that a single uncharged complex Fe–FA is formed, then each value of $\tilde{n}$ may yield two constants corresponding to equilibria:

$$Fe^{3+} + 3L^- = FeL_3 :$$
$$\beta_{Fe} = (FeL_3)/(Fe^{3+})(L^-)^3, \tag{12}$$

and

$$Fe^{3+} + 3LH = FeL_3 + 3H^+ :$$
$$\beta_{Fe}^H = (FeL_3)(H)^3/(Fe^{3+})(LH)^3 \tag{13}$$

The values of constants β_{Fe}^H and β_{Fe} may be calculated from the values of $\tilde{n}$ with the help of following relationships (Young et al., 1982):

$$\beta_{Fe}^H = \tilde{n}/(3 - \tilde{n})[(LH)/(H^+)]^3 \tag{14}$$

$$\beta_{Fe} = \beta_{Fe}^H(H^+)^3/(K_{APP})^3 \tag{15}$$

The applicability of this method is valid only when: (i) the assumption that the complex formed is uncharged $(3 - x = 0)$ is true, and (ii) the electrostatic charge on the polymer is a direct function of α_L. These two conditions may be achieved by mixing very small amounts of metal cation in concentrated ligand solution so that all the three charges of Fe^{3+} are coordinated by the ligand.

Materials and methods

Fulvic acids (FA)

Sludge from the sewage sludge treatment plant of Patna (India), farmyard manure (FYM), poultry manure (PM) and sulfitation pressmud (SPM) (waste of sugar industry manufacturing sugar by sulphitation process) were collected. These organic wastes are utilized for crop production as a source of plant nutrients. The air-dried and pulverized organic wastes were extracted separately with 0.1 M sodium pyrophosphate solution containing 0.1 M KOH for fractionation of fulvic acid. A modification of fractionation procedure of Kononova (1966), as described in detail by Pandeya (1992), was followed. The alkaline extract was acidified with H_2SO_4 to a pH of 2.0 for coagulation of humic acid gel. The sol of the fulvic acid so obtained was adsorbed on an acidified charcoal column. A modification of Forsyth's (1947) procedure was followed for purification of the fulvic acid. The fulvic acid adsorbed on the proton saturated charcoal column was washed with 0.5 M H_2SO_4 until free from metal impurities. A negative test for Fe^{3+} with potassium thiocyanate (KSCN) was used as an indication of purity. The charcoal in the column was then washed with distilled water to free it from sulphate. The fulvic acid was desorbed from the charcoal column by eluting it with 4 M NH_4OH until the liquid coming out had a pale straw colour. The fulvic acid so obtained was heated under reduced atmospheric pressure on a water bath at not more than 45 °C until free ammonia was removed. It was then filtered and passed through a series of columns, half filled with hydrogen saturated cation exchange resin (Dowex 50-X8, 20–50 US mesh, BDH chemicals, UK) until it attained a constant pH. The purified fulvic acid was stored in nitrogen atmosphere at 2–5 °C in coloured bottles.

In the absence of reliable data on the molecular weight of fulvic acid, an approximation of the mol-

arity of the fulvic acid was made from the threshold value for flocculation of Fe-fulvate on the assumption that fulvic acid forms a mononuclear insoluble complex with Fe^{3+} (Blaser et al., 1980; Pandeya, 1991). The approximation of molarity of fulvic acid was determined by discontinuous titration of fulvic acid with standard $FeCl_3$. The amount of $FeCl_3$ which just failed to produce turbidity in FA solution was taken as the end point of titration. The 50 mL aliquots of FA were dried in a water bath at 40–45 °C under vacuum to determine the quantity of fulvic acid present in the solution.

Reagents

Deionized and double glass-distilled water, stored in nitrogen atmosphere, we used to prepare all solutions. A working solution of KOH was prepared and its strength was determined accurately to the third decimal point by titration against standard H_2SO_4.

Apparatus

The instrument assembly employed for titration consisted of a digital pH meter with a combination glass-calomel electrode. The electrode was standardized using freshly prepared buffer solutions of pH 4.0 and 9.18. A beaker of 250 mL capacity, fitted with electrode, inlet and outlet tubes for N_2 gas and microburette on a rubber bung was used for potentiometric titration. A magnetic stirrer was used to homogenize the contents of the beaker during titration.

Procedure

A 50-mL aliquot of FA solution of 1×10^{-3} mol/L strength and 10 mL of 1 M KNO_3 solution were taken and the volume was made up to 100 mL with water. A nitrogen atmosphere was created inside the beaker by passing nitrogen gas through the inlet tube. The electrode of the pH meter was dipped into the solution and was allowed to stabilize until it gave a stable pH reading. An aliquot of 0.05 mL KOH (0.163 moles/L) was added to the FA solution and was stirred for at least 5 min. The pH of the equilibrated solution was recorded. This procedure was repeated with every increment of 0.05 mL KOH addition until the pH of the solution attained an equilibrium value of 11.0 or more. The same procedure of titration of FA in presence of Fe^{3+} was followed except that the FA solution contained a known amount of Fe^{3+}. The titration of all the four

samples of FA of different origins of the same strength was carried out without and with addition of Fe^{3+}.

The elemental composition of FA was determined by a CHN analyzer and the ash content was determined by ignition at 450 °C. The E_4/E_6 ratios of FA measured by taking the ratio of optical density at 465 and 665 nm wavelengths are informative indices of condensation of aromatic carbon network and the molecular size. Low values of E_4/E_6 are indicative of high aromacity due to humification. The contents of acidic functional groups like carboxyl and phenolic–OH were determined by potentiometric titration as described earlier (Pandeya, 1992).

Results and discussion

Fulvic acids extracted from different organic wastes showed wide differences in their chemical composition, aromacity, acidic functional groups and electrostatic properties (Table 1). The sources of fulvic acid did not only differ in terms of their total acidity, but also in the relative proportion of carboxyl group and phenolic-OH groups in different sources were different. The acidity of FA of FYM was predominantly due to carboxyl groups, whereas phenolic-OH groups contributed nearly one third of the total acidity in FA of sludge and poultry manure. Similarly, the values of pK_{INT} (apparent dissociation constant of carboxyl groups at $\alpha_L = 0.0$) and pKm (apparent dissociation constant of carboxyl groups at $\alpha_L = 0.5$) of FA sources differed widely among themselves. A higher value of the constant 0.868 nW indicates greater restrictions in dissociation of –COOH groups due to their close proximity, and little change in configuration of the macromolecules of FA during titration with alkali. Thus, the dissociation patterns of FA also dissimilar in different sources.

Titration curves

The initial pH of the fulvic acids of different sources ranged between 2.0 and 2.3. Upon addition of Fe^{3+} these solutions may undergo following two reactions.

(a) A small fraction of added Fe^{3+} may be hydrolysed. Theoretically, the ratio of the dominant hydroxy species of iron $Fe(OH)_2^+$ and Fe^{3+} may range between 1×10^{-3} and 1×10^{-2} (Langford and Khan, 1975) in the pH range under investigation. The aqueous system of fulvic acid, however, even at pH in the range of 2.0–2.3, contains a substantial amount of dissociated
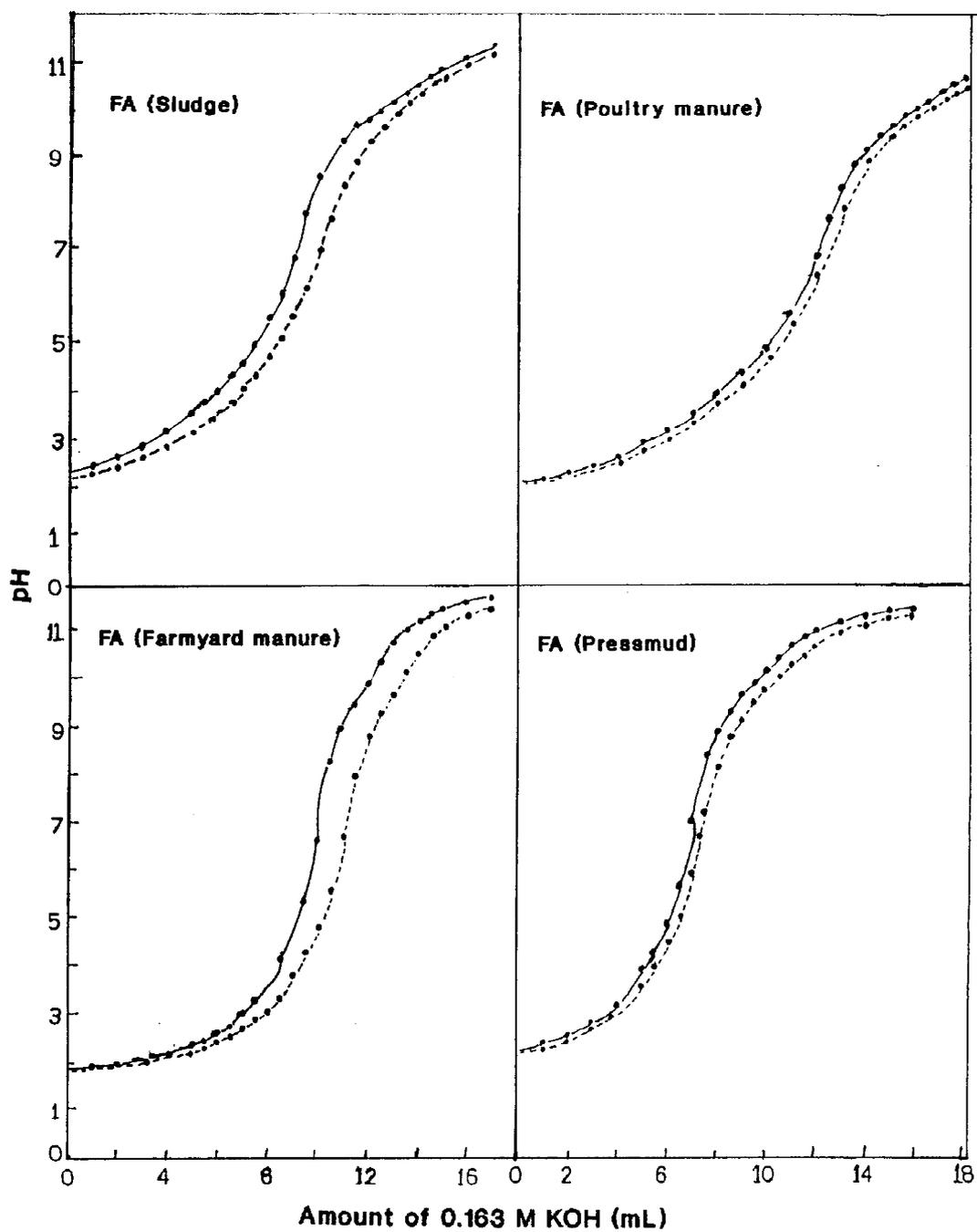
Figure 1. Potentiometric titration of fulvic acids in the absence (–) and presence of (- - -) of Fe^{3+}

Table 1. Analytical properties of fulvic acid (FA) extracted from organic wastes

Source of FA	Ash content (%)	Elemental composition (%)				E_4/E_6 [a] ratio	C:N ratio	Acidic functional group (mmol/kg)[b]			pK_{INT}	pK_{APP}	0.868 nW[c]
		C	H	N	O			Carboxyl groups	Phenolic –(OH)	Total acidity			
Farmyard manure	0.98	32.3	5.3	3.1	59.3	7.6	10.7	10155	1455	11300	2.31	2.62	0.62
Sludge	0.95	34.0	6.2	4.6	55.2	10.6	7.4	5070	992	6062	2.32	3.40	2.28
Poultry manure	0.95	32.8	5.5	6.5	55.2	8.5	5.0	5122	1247	6369	2.74	3.20	0.92
Pressmud	1.01	34.5	4.5	2.8	58.5	14.0	12.3	5623	1936	7559	2.39	2.97	1.25

[a] Ratio of optical densities at 465 nm and 665 nm wavelength.
[b] Estimated from potentiometric titration method (Pandeya, 1992).
[c] Electrostatic functions.

functional groups (pK_{INT}=2.31-2.74). As such, these functional groups are likely to compete with hydroxyl ions for Fe^{3+} and resultant hydrolysis of Fe^{3+} is likely to be too small to be considered. Chem and Gamble (1974) and Hargrove and Thomas (1982) in their studies on stability constants of metal–FA complexes also ignored the hydrolysis of metal cations at low pH values. It has also been demonstrated by Goodman et al. (1991) by Mossbauer spectroscopy that in a mixture of Fe(III) and fulvic acid of ratio 1:100 all the Fe^{3+} ions are complexed. The hydrolysis of iron is possible only when some uncomplexed Fe^{3+} is present in the solution and the pH is raised beyond 2.0. To make sure that all the Fe^{3+} in the solution remains complexed, the ratio of Fe^{3+}–FA was kept to approximately 1:100.

(b) Fe^{3+} will form a complex with fulvic acid ligands which will be accompanied by a drop in the pH of the system. The drop in the pH of the solutions may thus be attributed to the formation of fulvic acid iron complexes and release of protons from the functional groups (Khanna and Stevenson, 1962; Young et al., 1982). The potentiometric titration curves of fulvic acids in the absence and the presence of Fe^{3+} show that at all the points of titration curves, the pH of the fulvic acid iron complex was less than the corresponding pH of fulvic acid alone (Figure 1). In the zone within first inflection point of the titration curve, with every increment of KOH addition, the gap of pH between two conditions of titration increases. These observations signify that additional functional groups are dissociated to complex metal cations. The initial gradual rise in the pH with added KOH reflects buffering due to weak dissociation of –COOH groups (Sposito and Holtzclaw, 1977). This was followed by a sharp rise in pH of the medium, indicating neutralization of the carboxyl groups. The buffering zone during dissociation of functional groups of the fulvic acids was observed to extend in the pH range up to 4.5–5.0 with their complete neutralization at pH 7.0 in FA (pressmud) and 8.25 in case of FA (FYM). The pH of neutralization differed widely depending upon the origin of the fulvic acids. This indicated that the acidic functional groups, dissociating in this pH range, are not similar in nature. Such a behaviour of fulvic acid polymers has been attributed to configurational changes of these molecules on the expansion of macromolecules with an increase in pH of the titration medium. It is also possible that all –COOH groups are not present in such a steric disposition as to undergo simultaneous dissociation during titration with an alkali. A second buffering zone in the titration curve of fulvic acids extending over alkaline pH range and neutralizing at pH 10–10.5 was observed. This buffering zone due to weak dissociation of phenolic-OH group was not considered in the study.

The data obtained from the potentiometric titration of FA without addition of Fe^{3+} were analyzed according to Equation(4), and apparent dissociation constants (pK_{APP}) were calculated at different degrees of dissociation (α_L). Plots of pK_{APP} vs α_L are shown in Figure 2. According to Equation (4), if nW α_L is constant, the plots should have been straight lines with intercepts equal to pK_{INT} and the slopes equal to 0.868 nW. The plots obtained, however, were non-
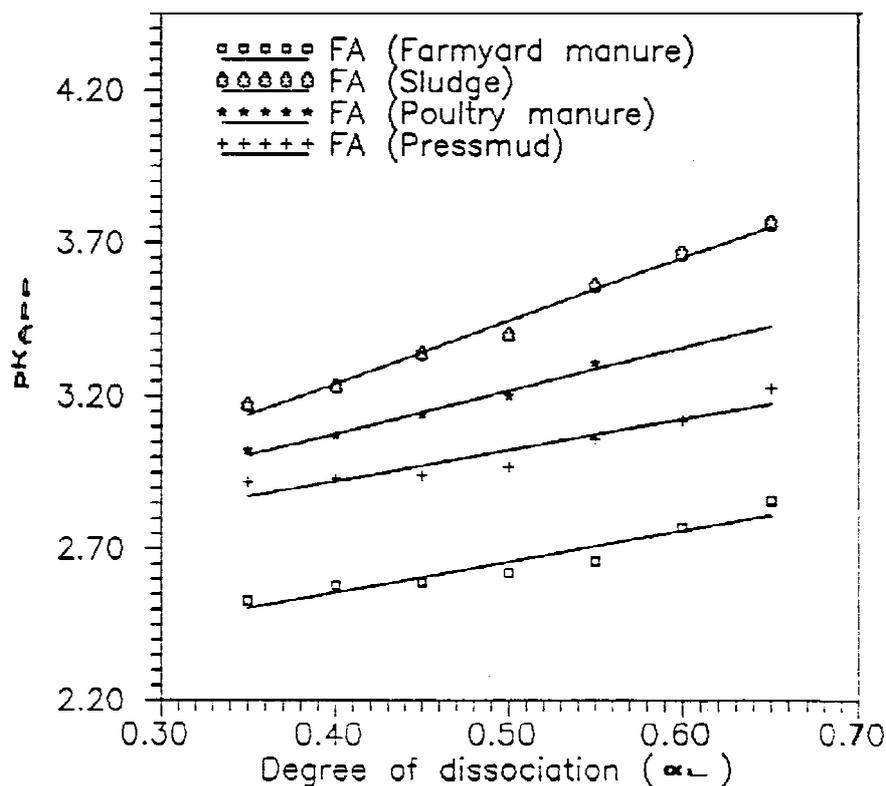
Figure 2. Change in apparent dissociation constant (pK$_{APP}$ on change of degree of dissociation (α_L).

linear at low and high α_L values but were linear in the mid range of titration curves with values of coefficients of determination above 0.95**, except for FA (sludge) where r^2 was equal to 0.73*. The clustering of undissociated –COOH on the coiled structure of fulvic acid molecules, leading to strong initial buffering, might have caused the deviations from linearity at low α_L values. Likewise, the presence of dissociated functional groups in the immediate vicinity of an undissociated functional group might resist further dissociation, which might have caused non-linearity at high α_L values. The analysis of the data for the calculation of stability constant of Fe–FA complex was, therefore, confined to α_L values to which pK$_{APP}$ − α_L followed linear relationships.

A decline in the values of the undissociated – COOH with increase in degree of dissociation in fulvic acids mixed with Fe^{3+} was observed (Table 2). This suggests enhanced complexation of metal cations by the functional groups at increasing pH values of the medium. Rapid reduction in the values of dissociated ligand –COO$^−$, approaching zero with increase in α_L

in case of FA (sludge), indicate its ability to expose dissociated ligands assessable of Fe^{3+}.

Bjerrum formation function ($\tilde{n}$) for formation of Fe–FA complexes, which indicates the average number of ligand molecules bonded to one Fe^{3+} increased with an increase in the values of α_L. Values of $\tilde{n}$ above three, estimated in case of fulvic acid from poultry manure, seem to be due to analytical error at high FA and low Fe^{3+} concentrations as the maximum number of ligands that theoretically may be involved during complexation of Fe (III) cannot exceed 3. Such unexpected results for values of $\tilde{n}$ have also been observed by Young et al. (1982) in their studies on the complexation of divalent metal cations by polycarboxylates. Therefore, calculation of β_{Fe}^{H} and β_{Fe} was kept confined to the most possible range of $\tilde{n}$ between 1 and 3. The calculated values of β_{Fe}, the stability constants of metal complex formation (Table 2) suggest that carboxyl groups of FA extracted from poultry manure complex Fe^{3+} with greatest affinity (log β_{Fe}=7.482–7.256) closely followed by FA from pressmud (log β_{Fe}=7.550–6.751), FYM (log β_{Fe}=7.453–6.156) and sludge (log β_{Fe}=6.558–5.639).

Table 2. Values of formation function $\tilde{n}$ and stability constant β_{Fe} at different degrees of α_L estimated by potentiometric titration of FA in presence of Fe^{3+}

α_L	pK_{APP}	$\tilde{n}$	$p\beta_{Fe}^{H}$	Log β_{Fe}
Farmyard manure 0.87 nW=0.62				
0.35	2.53	1.74	0.029	7.453
0.40	2.58	1.69	0.128	7.059
0.45	2.59	1.72	0.266	6.875
0.50	2.62	1.76	0.352	6.698
0.55	2.66	1.63	1.832	6.156
Sludge 0.87 nW=2.28				
0.35	3.17	1.07	1.928	6.558
0.40	3.23	1.09	2.344	6.318
0.45	3.34	1.14	2.673	6.138
0.50	3.40	1.19	3.074	5.986
0.55	3.56	1.27	3.498	5.871
0.60	3.67	1.35	3.964	5.768
0.65	3.77	1.44	4.508	5.695
0.70	3.98	1.54	5.107	5.639
Poultry manure 0.87 nW=2.28				
0.35	3.02	2.68	1.154	7.303
0.40	3.07	2.78	1.372	7.256
0.45	3.14	2.94	1.146	7.482
0.50	3.20	3.12	–	–
0.55	3.31	3.35	–	–
Press mud 0.87 nW=1.25				
0.40	2.92	1.98	0.568	7.550
0.45	2.94	1.99	0.875	7.345
0.50	2.97	2.05	1.079	7.140
0.55	3.06	2.12	1.283	7.005
0.60	3.12	2.19	1.602	6.869
0.65	3.23	2.27	2.043	6.751

The electrostatic functions of fulvic acid macromolecules, i.e. the values of 0.868 nW, seem to determine the affinity of the carboxyl groups for Fe^{3+} ($r=0.86^*$). Natural humic substances with higher –COOH density might be expected to have higher binding energy for metal cations as they have a greater number of chelate sites. This expectation, however, does not hold true in the present investigation. It is possible that high –COOH density on the fulvic acid macromolecules is accompanied by an increase in the chemical dipole effect over high-binding –COOH groups producing low pK_{APP} values, not favourable for cation bonding with stronger force (Pandey, 1992). This is why

a high molecular weight humic acid with low charge density has been reported by Stevenson (1977) to complex metal cations more strongly than highly acidic low-molecular-weight fulvic acids.

The stability constants of metal FA complexes are dependent upon the pH of the medium (Chem and Gamble, 1974; Gregor and Powell, 1986; Hargrove and Thomas, 1982; Langford and Khan, 1975; Sposito et al., 1978). However, in an electrostatic model of estimation polymeric charge or degree of dissociation remains the determining factor regardless the pH of the medium. A range of values, rather than a single value, of stability constant is obtained by this procedure. This result is more appropriate in a situation where no two carboxylic functional groups have similar electrostatic properties and the complexation of a metal cation by each of them will be with dissimilar energy. The nature of the binding of metal cations may also change with change in the values of α_L as $\tilde{n}$ increases with an increase in α_L. As such, the range of values of stability constants is expected to be more informative rather than a single value, lumping together the values at different stages of titration.

The stability constants of Fe–FA complexes in the present investigation have been calculated with only –COOH groups considered as complexing sites. The –COOH groups of fulvic acids extracted from the organic sources under study dissociate completely when the pH of the system attains a pH range of 7.00–8.25. No other functional group such as phenolic-OH or amides, will participate in complexation of metal ions till all the carboxyl functional groups are in the dissociated state or are occupied with the metal cation. This is because of the fact that the dissociation of these functional groups is possible only in the pH range of 8–10.5. The pH of the root environment in soils is usually acidic. As such, the contribution of phenolic-OH or of the amides present in fulvic acids in complaxation of Fe^{3+} is not expected to be high. Thus, the values of stability constants for formation of Fe–FA complexes by the fulvic acids of organic manures and wastes under study represent the values which may be expected in the soil environment on application of these wastes to soils. Relatively large values of the stability constants of Fe–FA complexes obtained in this investigation in comparison to those with competing metal cations in soils like Ca^{++}, Mg^{++}, Zn^{++}, Cu^{++} etc. as reported in literature (Stevenson, 1982), indicate that Fe^{3+} may effectively compete for FA ligands with other cations in the soil environment. Stable complexes of iron with humic matter are expected to be

formed upon incorporation of the organic manures and wastes in soils.

The chemistry of the complexes of Fe with fulvic acid has remained enigmatic so far on several accounts. Most of the data on stability constants of Fe–FA complexes are limited to those estimated at acidic pH ranges. The problem of the Fe deficiency and, therefore, the problem of augmenting Fe supply to crops arises in soils with neutral to alkaline pH. The effectiveness of Fe sources complexed with humic matter in enhancing the Fe availability to plants can best be known if data on stability constants of Fe-humic matter complexes are available for the pH ranges of soils. The data on the stability constants of Fe–FA complexes reported in the present form will, therefore, be useful in understanding the complexities of Fe supply to crops. The estimated values of stability constants for Fe–FA complexes are conditional and are true for set conditions of environment. Nature of the complexing ligands and pH and ionic strength of the aqueous media largely influence the stability of the complexes. The conditions prevailing in the experimental situations, however, may be encountered in most of the soil environments. Thus, the results may be applicable to understanding processes in soils and metal uptake by plants.

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