

SUMMARY AND CONCLUSION

In the introductory part of the thesis a brief review of the previous works on humus substances with regard to their composition, isolation from soils, fractionation, determination of molecular weights, conductometric and potentiometric titrations with different alkalies, spectrophotometric and viscometric measurements has been presented. A short discussion on the nature of the interacting sites and the complexing property and chelation reactions of humic and fulvic acids with different polyvalent metallic cations together with various methods for the evaluation of stability data of these metal-organic matter complexes has also been reviewed in this chapter.

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The scope and object of the present investigation have been discussed in chapter II. The importance on the following has been emphasised:

(a) Distribution and nature of the humus in the hill-soils of the Eastern-Himalayan Region.

(b) Characterisation of the humic and fulvic acid samples obtained from different sources by means of spectroscopic, viscometric, polarographic and potentiometric studies.

(c) Behaviour of six divalent metal ions (viz. Cu^{++} , Ni^{++} , Co^{++} , Zn^{++} , Pb^{++} and Cd^{++}) towards humic and fulvic acids and the stability data of these organic matter-metal complexes.

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The experimental details have been described in Chapter III. It includes isolation, fractionation and purification of the humus. Aqueous solution of 0.50(M) NaOH has been used to extract humic and fulvic acid from the soils as well as from the peat humic acid sample (supplied by Fluka AG). The acid soluble fulvic acids have been separated by dilute HCl and then preserved as Ba-Salt. A model humic acid is prepared in the laboratory by the oxidative coupling procedure from a mixture of ammonium chloride and p-benzoquinone at pH 8.00. Humic acids from Raja-Rammohanpur soil as well as from the peat humic acid have been methylated using dimethyl sulphate as methylating agent in presence of K_2CO_3 in acetone.

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Chapter IV : Some of the physico-chemical characteristics of the organic components of twelve soils collected from places of varying altitudes (Foothills to 11200 ft. altitude) and climatological conditions have been examined. (i) Decrease in the clay content, (ii) increase in organic matter and (iii) increase in the proportion of easily extractable fractions of humus are some of the significant observations in the samples obtained from regions of gradual increase in altitude.

Experimental data on pH, carbon content, cation-exchange capacity, clay content, optical density etc. together with appropriate interpretations of the results are presented.

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Chapter V deals with the characterisation of the humic and fulvic acids isolated from two of the soils studied in Chapter IV along with those from other sources including a synthetic one.

The C, H and N contents of samples have been tabulated. It has been found that the fulvic acids have a comparatively lower C and higher ash content than the humic acids.

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The chapter is divided into four sections:

Section A : This includes the visible and infra-red spectra of the humic and fulvic acids. The visible spectra (Fig. 4A) are monotonous, with no characteristic absorption band; continuous decrease in the optical density with increasing wavelength are noticeable. The E_4 / E_6 ratio (ratio of the optical density at 465 nm and 665 nm) for the humic acids are lower than that for the fulvic acids indicating that the former have more condensed aromatic rings than the latter.

The infra-red spectra for all the humic and fulvic acids (Fig. 4A.2) have been recorded using 'mull' technique employing 'nujol' as mulling agent. The bands for aliphatic C-H stretching near 2900 cm^{-1} and for $-\text{CH}_2$ at 1450 cm^{-1} and 1400 cm^{-1} are not distinguishable because of the specific absorption bands of nujol in these regions. Some other important features, characteristic of the soil organic matter, have been revealed

by the aforesaid spectra. The absorption band near 3300 cm^{-1} observed in all of the spectra has been assigned to the hydrogen bonded -OH groups. The presence of this band in the spectra of methylated humic acids suggests that all the -OH groups in humic acids are not methylated with dimethyl sulphate. Absorptions in the region $1720\text{-}1730\text{ cm}^{-1}$ assigned to C = O of -COOH groups and C = O stretching of ketonic carbonyl groups are found to be relatively intense for the fulvic acids. Methylation of humic acids causes a decrease in the absorption band at 1630 cm^{-1} and a slight increase at 1720 cm^{-1} . The Si-O-Si and Si-O-O valence and deformation vibration bands at 1050 to 1150 cm^{-1} are observed in all the spectra except in the synthetic one. This explains the ash content of the samples.

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Section B deals with the viscometric investigations of the samples. All the substrates exhibited typical behaviour of polyelectrolytes as indicated by their reduced viscosity vs concentration curves. The upward rise of the reduced viscosity with dilution is due to the intramolecular repulsion as a result of the dissociation of the ionisable groups accompanied with the maximum possible charge separation.

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Section C: It has been observed that all the humic and fulvic acid samples produce polarographic waves at a lower pH region. At higher pH region, the waves disappear. A more detailed investigation is warranted in order to identify the possible electroreducible groups in these acids.

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Section D: The potentiometric titration curves of humic and fulvic acids with KOH indicate their polybasic character even in presence of 0.1(M) KNO_3 . Amongst many, two distinctly separate inflexion points are observed in all cases except when the titrations are carried out in presence of 1(M) KNO_3 . In the latter case, the curves exhibit closely the strong acid behaviour. Thus the two major types of acidic groups in these acids have been assigned to : (a) Type I - the carboxylic acid groups, dissociating at a comparatively lower pH region, situated on the aromatic rings probably at the ortho position to the phenolic -OH groups and (b) Type II - weak -COOH groups and the phenolic -OH groups having higher pK values.

The Henderson-Hasselbalch equation as modified by Katchalsky and Spitnik for a polymeric acid is obeyed within a pH range (pH 4 to 6). These curves show vertical and almost parallel displacement on increasing the concentration of the neutral salt from 0.05 to 0.10 M. The pKa values as determined from the corresponding Henderson-Hasselbalch curves, ^{within} lie 4.85 to 5.31 for the humic acids including the methylated

samples and from 4.03 to 4.75 for the fulvic acids at an ionic strength of 0.10. The neutralisation pH is determined from a plot of $\Delta \text{pH}/\Delta \text{ml}$ of base added against pH and is taken as the point where $\Delta \text{pH}/\Delta \text{ml}$ shows the maximum value. For the fulvic acid this pH lies within 7.05 to 7.60 and that for the humic acid within 7.30 to 8.20 in presence of 0.10(M) KNO_3 . A little increase in the neutralisation pH is observed for the methylated humic acids (SMHA and PMHA) when compared with the corresponding free humic acids (SHA and PHA). Total acidity, as determined from the neutralisation point on the titration curves, is always higher for any sample when titrated in presence of a greater amount of KNO_3 . This may be attributed to the fact that on addition of increasing amount of the salt, the acidic groups which were shielded from neutralisation possibly due to the macromolecular conformation of the acids become increasingly available as more and more neutral salts are added. Considerable decrease in the total acidity is observed in the methylated humic acids (SMHA and PMHA) when compared with the original humic acids (SHA and PHA) due to the blocking of the -OH groups in the former, thus indicating a definite contribution of these -OH groups towards the total acidity of these substrates.

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Studies on the interaction between six divalent metallic cations and humic as well as fulvic acids have been

carried out with the help of potentiometric measurements (Chapter VI). The results have been considered from four different points of view:

i) Variation of pH of the humic substances on the addition of metal ions.

It has been observed that when a divalent metallic cation (e.g. Cu^{++} , Pb^{++} , Ni^{++} , Co^{++} , Cd^{++} or Zn^{++}) is added to these substrates at a particular pH, there is always a considerable drop in pH. The pH drop originates from the release of H^+ from the undissociated acidic groups (HA) of these weak polymeric acids and the higher is the extent of pH drop with a metal, the greater is its tendency to form the complexes. Based on this index, Cu^{++} and Pb^{++} ions are found to have much stronger affinity for the acidic groups of the humic or fulvic acids than Ni^{++} , Co^{++} , Cd^{++} and Zn^{++} . In general, the pH drop on addition of a metal ion is always lower for **fulvic** acids than for the humic acids. On increasing the concentration of metal ions pH drop further increases and ultimately remains more or less constant. This indicates that the tendency to combine with metal ions diminishes as the available interacting sites get rarer.

ii) Consumption of base by the acids released.

The amount of alkali consumed by the acids released, on addition of a particular metal ion, is a measure of its interaction with the substrate. But at pH 5 or 6, with Cu^{++}

and Pb^{++} , the quantity of alkali consumed is greater than the amount of the undissociated acidic groups (HA) from which the H^+ ions are liberated after the addition of metal ions. This indicates the existence of some apparently unaccountable H^+ which may be explained in the following manner, either,

(a) There are some very weak acidic groups which are not accessible for neutralisation with KOH under the conditions of the titration, but yield to the stronger complexing tendency of Cu^{++} and Pb^{++} .

or,

(b) Water molecules already bound covalently to the metal ions may be dissociated to produce some extra H^+ in the system.

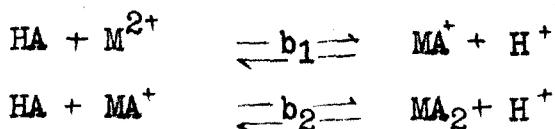
From the study it seems that both of these mechanisms are simultaneously probable, the former predominating at a lower pH whereas the latter at the higher pH region. The existence of such unaccountable H^+ is not observed with other metal ions like Ni^{++} , Co^{++} , Zn^{++} and Cd^{++} . At lower pH, the metal ions cannot bind ~~with~~ all the sites which are available for interaction, possibly due to the competition between the H^+ and the metal ions for the reacting sites.

iii) Stability Constants.

The stability constant values have been calculated following the approach of Gregor et al (1955) as modified by Stevenson (1977). It has been considered that the metal

ions are bound to the dissociated acidic groups and in such cases a competition between the metal ions and H has been taken into account. The dissociation equilibrium of the acids are assumed to be unaffected by the formation of a complex. In evaluating stability data adopting the method of least square, only the experimental values at a lower concentration of metal ions have been considered so that the values obtained may represent those involving the stronger sites.

A two-step equilibrium has been considered:



and the over-all formation constant B_2 for the complex MA_2 is given by

$$B_2 = b_1 b_2 = \frac{(\text{MA}_2)(\text{H}^+)^2}{(\text{M}^{2+})(\text{HA})^2}$$

The constants B_2 are finally transformed into a more commonly expressed constant K_2 by the relation

$$b_1 = K_a k_1$$

$$\left(\text{Notably, } K_2 = k_1 \cdot k_2 = \frac{(\text{MA}_2)}{(\text{M}^{2+})(\text{A})^2} \right),$$

where K_a = dissociation constant of the acid HA

b_1 and k_1 are the successive stability constants.

The stability or formation constant data (both $\text{Log } B_2$ and $\text{Log } K_2$) obtained in the present investigation are in close

agreement with the Irving-Williams series for the stability of metal chelates. This suggests that the chelates are formed during interaction of these divalent metal ions with humic and fulvic acids. The values obtained are in corroboration with the findings of many earlier workers.

iv) Mechanism of interaction

Considering the structural aspects of these acids as well as the relative position of the acidic groups, it may be concluded that both phthalic acid type and salicylic acid type of chelates are possible. As it is seen that the stability constants of metal-humic acid complexes are little affected even when the -OH groups are blocked with methyl groups, the probability of phthalic acid type of complex formation with the unmethylated acids seems considerably high. Nevertheless, the possibility that salicylic acid type of chelates are also formed cannot be altogether ignored.

The formation of a 2:1 type of complex would always result two negative charges on the complex itself. Such anionic complex under normal condition should not be reduced at the dropping mercury electrode. It has been observed in our laboratory that at all level of metal/2HA ratio studied, the nature of the wave as well as the half wave potential are almost unchanged when these complexes are subjected to polarographic studies. This strongly suggests that 1:1 complexes are probably

formed. 2:1 complexes, if formed at all, are weak and attain the suitable configuration so as to give the normal cathodic wave. No indication is, however, available as to the participation of the groups like $-NH_2$, $=NH$, $-C=O$, etc. in the formation of a complex with these metal ions.