CHAPTER II

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From the introductory review on humic acid investigations it appears that despite the vast amount of work already carried out on different aspects of humic acids their constitution and physical and chemical properties remain today largely unknown. The elucidation of the molecular structure of the chemical entities which are grouped together under the general term, humus, is really a problem which is organo-chemical in nature. In the present work we have not dealt with this aspect of the problem. But we have tried to elucidate partially the peripheral structure of humic and fulvic acids. To achieve this object and to find out whether humic and fulvic acids are structurally similar or different, a study on the infra-red spectra of fractionated humic and fulvic acids has been undertaken. The currently prevailing theories of humus genesis in soils and peats have been examined in the light of the infra-red data obtained in the present work and by other workers.

The difficulty in characterizing humic and fulvic acids and in exploring their physicochemical properties is attributed to the extremely heterogeneous nature of the soil organic matter. Although several attempts have been made to resolve humic acids by the application of modern methods of separation, no detailed study of the physico-chemical properties of these fractions has been carried out. In the present work we have made some attempts to fractionate the components of soil humus...
by chemical and chromatographic techniques (adsorption column chromatography and paper electrophoresis) and have studied them by a number of physico-chemical methods. The suitability and efficiency of the chromatographic techniques in resolving humic acids have been discussed.

Humic and fulvic acids are known to fluoresce both under ultraviolet and visible light. Although this property has been utilised by a number of investigators in studying the progress of fractionation of humic acids on chromatographic papers and columns, a quantitative investigation of this important property as also spectral distribution of fluorescence colour of humic and fulvic acids has not been made. The present work attempts to investigate fluorescence property as a possible means of characterizing humic and fulvic acids. With this object in view spectral distribution of fluorescence colour of humic and fulvic acids has been studied. Simultaneously a discussion on the skeletal structure of the fluorophor responsible for the observed fluorescence has been made.

Humic acids are strongly coloured substances. Some type of chromophoric group is responsible for this dark colour of humic acids. Accordingly the presence in humic acid molecule of an extended conjugated quinonoid structure has long been postulated. Chromophores are very often characterized by their electronic spectra. Hence, with the object of characterizing the group or groups responsible for the dark colour of humic acids, the light absorption properties of humic and hymatomelanic acids both from soil and compost and of soil fulvic acid have been investigated over the whole
U.V. and visible regions of the electromagnetic spectrum (from 2300 Å to 5500 Å).

It has long been assumed that humic acid has a highly condensed ring structure which would be expected to result in a relatively rigid molecule. This belief has recently been refuted on the basis of viscosity measurements by a number of investigators who hold that humic acids isolated from diverse sources are essentially flexible polyelectrolytes in character. However, observations made in this field are mutually contradictory. To examine the above view, viscometric study on sodium humate has been undertaken. An attempt has been made in terms of intrinsic viscosity to establish the possible molecular configurations of humic acid. Some calculations regarding the possible shape and size of different humic acid preparations have been made from the published data on the intrinsic viscosity, partial specific volume, sedimentation and diffusion constants of humic acids to show how the values of the molecular parameters come out to be if the above data are interpreted in terms of different molecular models.

The introductory review further reveals that in spite of considerable work carried out on the electrochemical properties of humic acids, differences of opinion exist as (a) the acid character of humic acid, (b) the mechanism of interaction of humic acid with neutral salts, and (c) the nature of conductometric and potentiometric titration curves. The present work aims at having fuller informations on these points and to explore the possibility of characterizing humic and fulvic acids by measuring their initial pH values and initial conductances under comparable concentrations.
It is well known that the properties of humic acids vary with soil conditions. Humic acids isolated from a tropical mineral soil will differ from those isolated from a peat soil, since in the latter the organic matter is at the beginning of the decomposition process, whereas the mineral soil organic matter may be considered to be in a much advanced stage of decomposition. It would, therefore, be highly interesting to compare the data obtained by us for mineral soil organic matter with those already published for peat organic matter and to find out their similarities or dissimilarities, if any. Available data on mineral soil organic matter are also recorded for comparison.

Therefore, in brief, the present investigations on humic and fulvic acids isolated from a typical mineral soil and on humic acids isolated from a compost soil have been largely centered around the following topics:

(1) Isolation and chemical analysis.
(2) Electrochemical properties: Characterization by (i) potentiometric and (ii) conductometric titration curves.
(3) Spectral analysis: (1) Fluorescence Emission spectra, (ii) Absorption spectra, (iii) Infra-red spectra.
(4) Hydrodynamic behaviour.