

II. CHEMISTRY

Soil Chemistry

STUDIES ON THE VISCOMETRIC BEHAVIOUR OF NATURAL, SYNTHETIC AND MICROBIAL HUMIC ACIDS

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A comparative study has been made on the viscometric property of natural, synthetic and microbial humic acids together with their nitro and sulphonated products. Polyelectrolytic character is observed in all the cases. The viscosity average molecular weights is found to follow the order "natural > microbial > synthetic." Significant effect of *pH* on the molecular weight of FA is noticed. Temperature also affects the viscometric property of HA.

Key words: Humic acid; Fulvic acid; Polyelectrolyte behaviour; Viscosity studies.

INTRODUCTION

VISCOMETRIC method (Rajalakshmi *et al.*, 1959; Piret *et al.*, 1960; Datta & Mukerjee, 1970; and Chen & Schnitzer, 1976) has been used to characterize humic acids by earlier workers. The polyelectrolytic behaviour of coal humic acid have been established by Mukherjee and Lahiri (1956) and Rajalakshmi *et al.* (1959). Besides polyelectrolytic nature, non-sphericity of humic acid molecule has been shown by Piret *et al.* (1960), but Flaig and Bentelspacher (1954) showed from viscometric measurements that both natural and synthetic humic acids are more or less spherical in shape. Attempts have also been made by some workers (Wershaw *et al.*, 1967; and Khan, 1971) to co-relate two conflicting theories and they are of the opinion that humic acid is composed of a mixture of both linear and spherocolloid and the particles of humic acid vary both in size and in shape.

Recently, Chen and Schnitzer (1976) have attempted to get informations on the shape, size and molecular weights of humic acid and fulvic acid molecules under varying *pH* from viscometric studies and have shown that molecules of HA/FA form aggregate at low *pH* and disperse at higher *pH*.

In the present paper, viscometric behaviour of humic acid isolated from pond sediment has been compared with those prepared by synthetic chemical and microbial processes. A comparison has also been made of their nitro and sulphonated products with their respective parent counterparts. Measurements have also been made at different *pH* values and in presence of neutral salt solution to get information of their effects on viscometric properties and molecular weights.

MATERIALS AND METHODS

The methods of the preparation of samples of natural, synthetic (chemical) and microbial humic acids and their nitro and sulphonated products have been stated

in earlier communication (Adhikari *et al.*, 1978). The supernatant liquid after precipitation of HA, was coagulated as the barium salt of FA by adding BaCl_2 solution at $p\text{H}$ 8.0. Barium fulvate was dialysed to make free from electrolytes. Fulvic acid was prepared by passing through Amberlite 120 H-resin before each experiment. Initial $p\text{H}$ for 0.6 per cent solution of FA was 3.05. Sodium humate solution was prepared by treating the dialysed HA suspension with a dilute solution of NaOH to $p\text{H}$ 8.0.

The viscometric measurements were done with the aid of an Ubbelohde viscometer with a flow time for distilled water being adjusted to 138.5 secs at $30 \pm 0.1^\circ\text{C}$ maintained in a water thermostat. In the cases of HAs and their derivatives, the measurement of viscosities were done at $p\text{H}$ 8.0 and in presence of 0.1 M NaCl. In case of FA, measurements were made at different $p\text{H}$ viz., 1.0, 2.0, 4.0, 7.0, 8.0 and 10.0 adjusted either with dil. HCl or NaOH. Besides 30°C , measurements of viscosities at two other temperatures viz. 40°C and 50°C were also made.

RESULTS AND DISCUSSION

The results obtained from the viscometric measurements are shown in Figs. 1 to 5. Tables I and II show the values of intrinsic viscosities $[\eta]$ obtained from the graphs and the molecular weights derived from these values by employing Staudinger's equation,

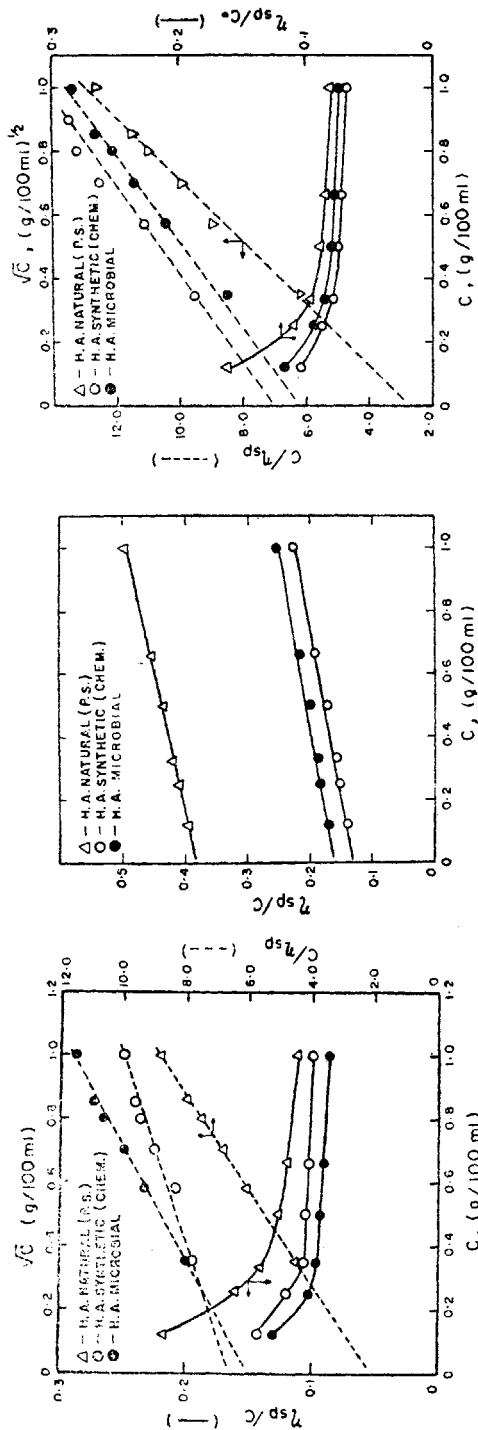
$$[\eta] = K\bar{M}_v^\alpha,$$

where K and α are constants. Taking the value of α to be 0.65 (a value followed by most of the flexible polyelectrolytes), the values of K for HA and FA have been calculated from the known values of the molecular weights determined by electro-metric method (Datta, 1968). The values of K for HA and FA samples thus obtained are 7.33×10^{-4} and 3.0×10^{-4} respectively.

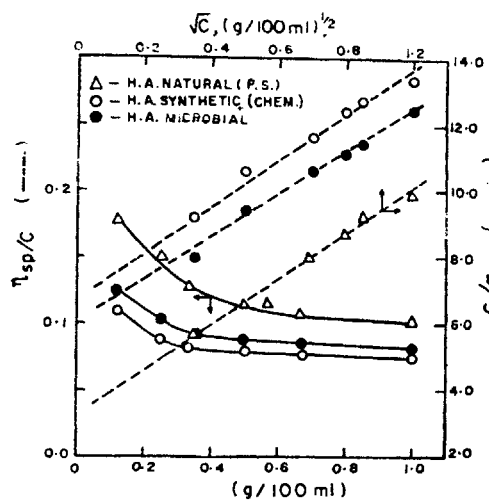
The typical plots of reduced viscosity (η_{sp}/c) vs. concentration (C) for natural, synthetic and microbial HA are shown in Fig. 1. The curves show the polyelectrolytic character for all the three types of HA. As the ionization of HA molecules increases with the gradual dilutions, the molecules repel each other and this causes a stretching of the macromolecular chain of HA. As a result an enormous rise in reduced viscosity occurs at high dilution. It then becomes very difficult to obtain the value of intrinsic viscosity ($\eta_{sp}/c = [\eta]$) from the plot of η_{sp}/C vs. and $\lim_{c \rightarrow 0}$

in such cases the reciprocal plot, that is c/η_{sp} is plotted against \sqrt{c} to obtain the reciprocal value of $[\eta]$ (Fuoss & Cathers, 1949).

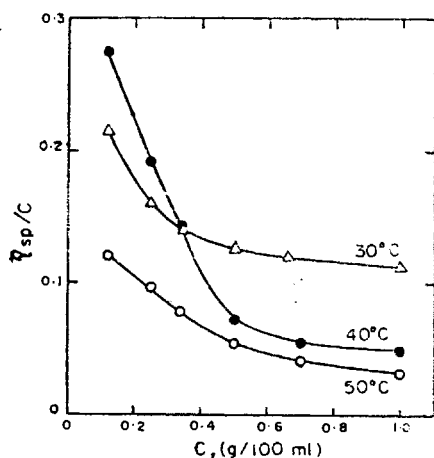
But on the addition of salts the ionization of HA molecules can be checked and the molecules behave as neutral macromolecules. $[\eta]$ values in such cases are easily obtained from the extrapolation of the reduced viscosity vs. concentration plots. The values of the intrinsic viscosities and the molecular weights calculated therefrom are shown in Table I. The results show that among the three types of HA, natural HA has the highest value of $[\eta]$ and molecular weight viz., 0.476 and 21,280 respectively followed by microbial and synthetic HA. Among the five



Figs. 1-3. 1. Plots of reduced viscosity (η_{sp}/c) vs. concentration (c) for natural, synthetic and microbial humic acid 2. Reciprocal plots i.e., c/η_{sp} vs. \sqrt{c} from Fig. 1. 3. Reduced viscosity vs. concentration plots of nitro production of humic acids.



(4)



(5)

Figs. 4-5. 4. Reduced viscosity vs. concentration plots of sulphonated products of humic acids. 5. Effect of temperatures on viscometric behaviour of natural humic acids.

synthetic HA, synthetic HA(C) that is, the humic acid prepared from glucose has the highest molecular weight and the synthetic HA(E) has the lowest value. Addition of neutral salt solution causes a lowering of the $[\eta]$ value as well as the molecular weight for all HA/FA samples. The lowering in the value of molecular weight is more than 6000 in case of natural HA whereas in the cases of synthetic and microbial HA, the values are only a few hundreds. The added salt neutralizes the charges on the backbone of the macromolecule and causes an enormous compression of the large hydrodynamic volume.

The reduced viscosity vs. concentration plots (Figs. 3 and 4 for nitro and sulphonated products) also establish their polyelectrolytic character and from the lower values of the intrinsic viscosities and molecular weights in comparison to their respective parent counterparts, it is inferred that they represent smaller molecules than their parent counterparts. The findings are also in agreement with the results obtained by other physico-chemical studies (Adhikari *et al.*, 1978). The molecular weights for nitro and sulphonated products of natural HA are found to be decreased by nearly 7000 and 10000 respectively while for other synthetic and microbial products such decrease is hundred or even less.

In case of FA, reduced viscosity vs. concentration plots (not shown) are similar to those of HA showing polyelectrolytic character. Intrinsic viscosities as obtained from the reciprocal plots and the calculated molecular weights are shown in Table II. The data in Table II show the effect of pH on the intrinsic viscosity and the molecular weight of FA. At very low pH viz., 1.0, FA has the highest value of $[\eta]$ and molecular weight viz., 0.089 and 6353 respectively. With increase in pH both parameters simultaneously decrease reaching the lowest value viz., 0.048 and 2460 respectively at pH 4.0 with further increase in pH , there is a gradual increase in the values of intrinsic viscosity and the molecular weight. The results establish more

TABLE I
 $[\eta]$ and molecular weight for humic acid and their derivative

Sample	$[\eta]$ in dl/g	Molecular wt.
Natural humic acid	0.476	21,280
Natural humic acid (in 0.1(N) NaCl)	0.378	14,894
Microbial humic acid	0.166	42,27
Microbial humic acid (in 0.1 (N) NaCl)	0.161	3,981
Synthetic humic acid (A)	0.153	3,750
Synthetic humic acid (A) (in 0.1 (N) NaCl)	0.140	3,221
Synthetic humic acid (B)	0.151	3,656
Synthetic humic acid (C)	0.158	3,926
Synthetic humic acid (D)	0.152	3,715
Synthetic humic acid (E)	0.150	3,589
<i>Nitro derivatives</i>		
Natural humic acid	0.37	14,388
Microbial humic acid	0.1603	3,890
Synthetic humic acid (A)	0.142	3,342
Synthetic humic acid (B)	0.1408	3,266
Synthetic humic acid (C)	0.155	3,784
Synthetic humic acid (D)	0.148	3,548
Synthetic humic acid (E)	0.146	3,443
<i>Sulpho derivatives</i>		
Natural humic acid	0.301	11,120
Microbial humic acid	0.162	3,982
Synthetic humic acid (A)	0.149	3,562
Synthetic humic acid (B)	0.1504	3,614
Synthetic humic acid (C)	0.156	3,828
Synthetic humic acid (D)	0.1501	3,597
Synthetic humic acid (E)	0.1485	3,532

TABLE II
 $[\eta]$ and molecular weight of fulvic acid at different pH

pH	in dl/g	Molecular weight
1.0	0.089	6353
2.0	0.072	4581
4.0	0.048	2460
7.0	0.054	2944
8.0	0.059	3372
8.0	0.044	2152
(in 0.1(N) NaCl)		
10.0	0.065	3917

rigidly the view as obtained from our earlier studies (Adhikari *et al.*, 1978) and also as stated by Chen and Schnitzer (1976) that at low pH, the molecules form aggregate through H-bonding, Van der Waals forces and other weak forces but with increase in pH, these forces become weaker and the aggregate breaks up. Thus at neutral pH, FA has the minimum molecular weight but at still higher pH, some sort of rearrangement of the fully ionized molecules may help regrouping of the molecules to form discrete particles which causes a small increase in molecular weight.

Temperature effect on viscometric behaviour at three different temperatures 30°, 40° and 50 °C for natural HA is shown in the Fig. 5. The polyelectrolyte behaviour is more pronounced at 40 °C than at 30 °C. This is due to increased ionization of HA molecule at higher temperature. At higher temperature viz., 50 °C, the values of reduced viscosity at a particular concentration are smaller than either of the value at other two lower temperatures. This is possibly due to the lowering of the viscous drag at higher temperature and at the same time due to the coiling of the molecules at the elevated temperature.

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