

II. CHEMISTRY

Soil Chemistry

INTERFACIAL PHENOMENA OF HUMIC SUBSTANCES

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The surface active property of natural, chemically synthesised and microbially synthesised humic substances together with their nitro and sulfonated products were studied both at air-water and oil-water interfaces. The number average molecular weights and the limiting film areas were calculated. On the basis of their molecular weight and the limiting film areas, the flexibility of the macromolecular chains are discussed here.

Keywords : Interface; Adsorption; Hydrophilic; Hydrophobic

INTRODUCTION

THE surface active properties of humic substances have profound influence on the fate of several agrochemicals in soil. Adsorption of these chemicals by humic substances controls the quantity of them in soil solution and thus determines their persistence, leaching, mobility and bioavailability. The extent of adsorption depends not only on the nature and properties of chemicals but also on the type and amount of organic matter present.

Soil humic substances contain both hydrophilic ($-\text{CO}_2\text{H}_2-\text{OH}$) and hydrophobic groups (aliphatic hydrocarbons, esters of fatty acids, aromatic rings) which impart on humic substances diverse surface active properties having both water holding (Scheffer & Ulrich, 1960) as well as water repellent capacities (DeBano and Letey 1969; and Adhikari & Chakraborty, 1976).

Several attempts have been made by the earlier workers (Chen & Schnitzer, 1978; and Ghosh *et al.*, 1971) to measure the surface area and hence to calculate the number average molecular weights in order to explain the different soil physical properties.

At high ionic strength of solution, the surface area of humic materials can be obtained by applying Gibbs equation.

$$\text{Surface adsorption } \Gamma = - \frac{1}{RT} \left(\frac{d\gamma}{d \ln c} \right) \quad \dots(1)$$

Γ = Surface adsorption (mole/cm²)

R = Gas constant

T = Absolute temperature

γ = Surface tension (dynes/cm)

According to Adam (1941), an ideal gaseous film of area 'A' will have the surface pressure

$$\pi A = nRT \quad \dots(2)$$

where 'n' is the number of moles. A substance having unknown number average molecular weight

$$\overline{Mn}, n = \frac{W}{\overline{Mn}} \text{ where } W \text{ is the weight of the film spread on the}$$

area A.

$$\therefore \pi A = \frac{W}{\overline{Mn}} \cdot RT \quad \dots(3)$$

In a real case, deviation from ideal behaviour occurs, hence modified form of Adam's equation is usually applied.

$$(\pi - \pi_0)(A - A_0) = nRT \quad \dots(4)$$

where π_0 is $(\pi)_{c \rightarrow 0}$ and A_0 is the limiting film area.

For large molecules no intramolecular attraction exist at low pressure i.e., $\pi_0 = 0$.

Therefore, the equation can be rewritten as

$$\pi A = \pi A_0 + nRT \quad \dots(5)$$

\overline{Mn} can be calculated from the intercept on the πA axis of the plot πA against π and the value of A_0 is obtained from the slope of the curve

In the present paper, attempts have been made to compare the surface areas as well as the average molecular weights of natural, microbial and chemically synthesized humic acids and their respective sulfo and nitro derivatives. The investigations were carried out both at air-water and at oil-water interfaces.

MATERIALS AND METHODS

The method of isolation and preparation of samples of natural, synthetic (chemical) and microbial humic acids and their nitro and sulphonated products have been stated in earlier paper (Adhikari *et al.*, 1978).

Surface tension measurements were carried out by a DUNOÛY type Tensiometer (USA) at a temperature of 25 °C using 20ml solution at each time. Surface tension values were measured both at A/W and O/W (n-heptone/H₂O) interfaces. An optimum depth of immersion (0.50 cm) was always maintained. The surface pressure π at each solute concentration has been calculated from the relationship $\pi = \gamma_0 - \gamma$ where γ_0 and γ are the surface tension of solvent and solution respectively. The γ_0 value of the solvent was 72 dynes/cm at 25 °C.

From the values of surface tension (γ) recorded at different concentrations (c) plots of ' γ ' vs. 'c' and ' γ ' vs. 'log c' were obtained. From the ' γ ' vs. 'log c' curve the value of $d\gamma/d \log c$ was calculated.

RESULTS AND DISCUSSION

The decrease in surface tension values with increase in concentration as has been observed in the plots γ vs. c (not shown in the paper) indicates the surface active

behaviour of humic substances. The decrease in surface tension value of water by addition of humic substances is due to adsorption at the surfaces. By calculating $d\gamma/d \log c$ from the curves (γ vs. $\log c$) the surface areas of humic substances both at A/W and O/W interfaces were calculated. The limiting film areas (A_0) of humic acids at O/W interfaces are slightly higher than at the A/W surfaces. The higher values obtained at the O/W interfaces are due to the electrostatic forces of repulsion and the dissolution of the polymer film in oil layer (Millar, 1954). Practically in the O/W interface certain amount of strain is imposed on the polymer molecules due to the different orientations of functional groups. The non polar groups are directed towards the oil phase while the polar groups enter into the aqueous phase (Davies & Rideal, 1963). To calculate the number average molecular weights (\bar{M}_n) of the humic acids, the graphical plots of πA against π have been made (Fig. 1), πA vs. π

- NAT HA (A/W)
- NAT HA (O/W)
- MICROBIAL HA (A/W)
- ◐—◐ MICROBIAL HA (O/W)
- △—△ SYN HA (A/W)
- ▲—▲ SYN HA (O/W)

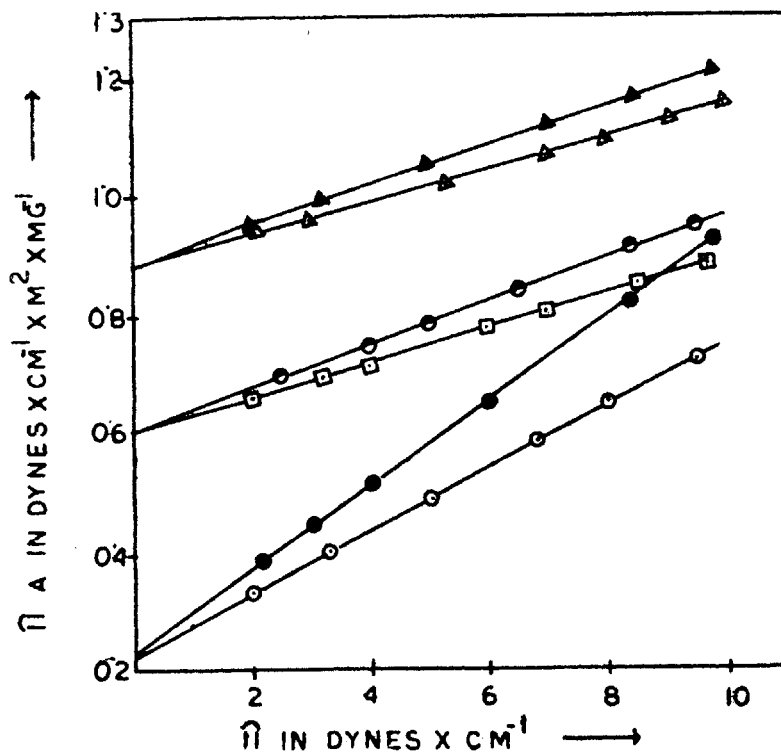


FIG. 1. πA vs. π .

curves are linear both at A/W and O/W interfaces for all the samples studied. The πA vs. π plots of any sample give the same intercept at the πA axis, but different slopes at A/W and O/W interfaces. By entrapulating the plots ($\pi \rightarrow 0$) the πA values have been obtained from the intercept and with the help of the eqn. (3), number average molecular weight of humic acids have been calculated.

From Table I, it is seen that all the natural, chemically synthesized and microbial humic acids have the molecular weight values same at the air-water and oil-water interfaces indicating the rigidity of the polymer film. The number average molecular weights (\bar{M}_n) follow the order :

Natural (HA) > Microbial HA > Synthetic HA.

TABLE I
Molecular weight and limiting film area

Sample	Molecular weight (\bar{M}_n)		A_0 in m ² /mg	
	A/W	O/W	A/W	O/W
HA (P. S.)	11083	11083	0.5	0.75
Synthetic HA (A)	2784	2784	0.265	0.321
Synthetic HA (B)	2656	2656	0.245	0.33
Synthetic HA (C)	2971	2971	0.275	0.38
Synthetic HA (D)	2718	2718	0.232	0.325
Synthetic HA (E)	2632	2632	0.235	0.317
Microbial HA (F _b)	3718	3718	0.285	0.357
<i>Nitro derivatives</i>				
HA (P. S.)	8214	8214	0.7	0.78
Synthetic HA (A)	2218	2218	0.25	0.36
Synthetic HA (B)	2137	2137	0.22	0.335
Synthetic HA (C)	2771	2771	0.291	0.41
Synthetic HA (D)	2521	2521	0.253	0.369
Synthetic HA (E)	2448	2448	0.24	0.395
Microbial HA (F _b)	2978	2978	0.29	0.40
<i>Sulpho derivatives</i>				
HA (P. S.)	7685	7685	0.85	0.91
Synthetic HA (A)	2190	2190	0.28	0.352
Synthetic HA (B)	2168	2168	0.255	0.378
Synthetic HA (C)	2641	2641	0.253	0.369
Synthetic HA (D)	2238	2238	0.278	0.382
Synthetic HA (E)	2371	2371	0.252	0.367
Microbial HA (F _b)	2875	2875	0.34	0.46

The number average molecular weights of all the sulphonated products of humic acids are higher than their respective nitro-derivatives. The average molecular weight of natural humic acid is the highest (11083) while the humic acid synthesized from catechol and alanine, i.e., humic acid (E) having the lowest value (2632). The average molecular weights of all the humic acids and their nitro- and sulphoderivatives

have lower values than their respective viscosity average molecular weights (Adhikari *et al.*, 1979). This indicates the heterogeneity of the systems. The limiting film areas of the humic acids do not follow the same trend like molecular weights. The sulpho derivatives of the natural humic acid have the highest surface area, which indicates that introduction of polar groups increases the spreadability of the molecules. All the sulphonated products of humic acids have higher surface areas than their nitro-derivatives and their parent humic acids except the humic acid (C) prepared from carbohydrate source (without nitrogen) where the nitro-derivatives have higher surface area than the sulphonated products.

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