

## **Hymatomelanic Acids as Polyelectrolytes.**

### **I. Viscometric and Osmometric Studies**

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#### **Synopsis**

The polyelectrolyte character of four natural and ten synthetic hymatomelanic acids, synthesized from possible monomers both in the presence and absence of catalysts, was established by means of viscosity measurements. Intrinsic viscosities were evaluated for the purpose of comparison. The number-average molecular weights of some typical natural and synthetic hymatomelanic acids were determined from osmotic pressure measurements. Using the Flory-Fox relationship in an approximate manner, the root-mean-square average end-to-end separations were also evaluated.

#### **INTRODUCTION**

Several investigators<sup>1,2</sup> have demonstrated the polyelectrolyte nature of coal humic acids by means of viscosity measurements. The polyelectrolyte character of peat humic acids was also demonstrated by Piret.<sup>3</sup> These observations are in direct contradiction with those made by Flaig and Beutelspacher,<sup>4</sup> who showed by means of viscosity measurements that both natural and synthetic humic acids are spherical in shape. Though recent investigations by Mukherjee and co-workers<sup>5,6</sup> have supported, by means of viscosity measurements, the polyelectrolyte nature of natural and synthetic humic and fulvic acids, very little so far is known about their alkali- and alcohol-soluble but acid-insoluble hymatomelanic acid fractions.

#### **EXPERIMENTAL**

##### **Preparation of Samples**

Hymatomelanic acids, the alcohol-soluble fraction of humic acids, were obtained from four typical Indian soils. They were converted into their sodium salts and designated as DRDN, PLPR, JBLP, and BRPR according to the respective place names of the soils.

Synthetic humus was prepared by persulfate oxidation and polycondensation of catechol in the presence or absence of glycine. The corresponding sodium hymatomelanates were designated as AN and A, respectively.

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Synthetic humus was also prepared by hydrochloric acid polycondensation of glucose in the presence or absence of glycine. The corresponding sodium hynamelanates were designated as CN and C, respectively.

Moreover, synthetic humus was prepared from catechol/glucose in presence of sand/silt or clay as possible catalysts. The corresponding sodium hynamelanates were designated as A (sand), A (silt), A (clay), C (sand), C (silt), and C (clay), respectively.

### Viscosity Measurements

Viscosity measurements of sodium hynamelanates were done with a Cannon-Fenske viscometer, having a flow time of 241.1 sec for 5 ml distilled water, in a water thermostat maintained at  $30^\circ \pm 0.1^\circ\text{C}$  by a toluene mercury thermoregulator operating in conjunction with an electromagnetic relay system.

The solutions, being very dilute, were assumed to have the same density as that of the solvent.

### Osmotic Pressure Measurements

The equilibrium pressure was determined after the Zimm-Meyerson-type osmometer had been left in the  $30^\circ \pm 0.02^\circ\text{C}$  thermostat for 15 hr. Necessary considerations for the osmotic pressure of the salt solution medium were also taken into account.

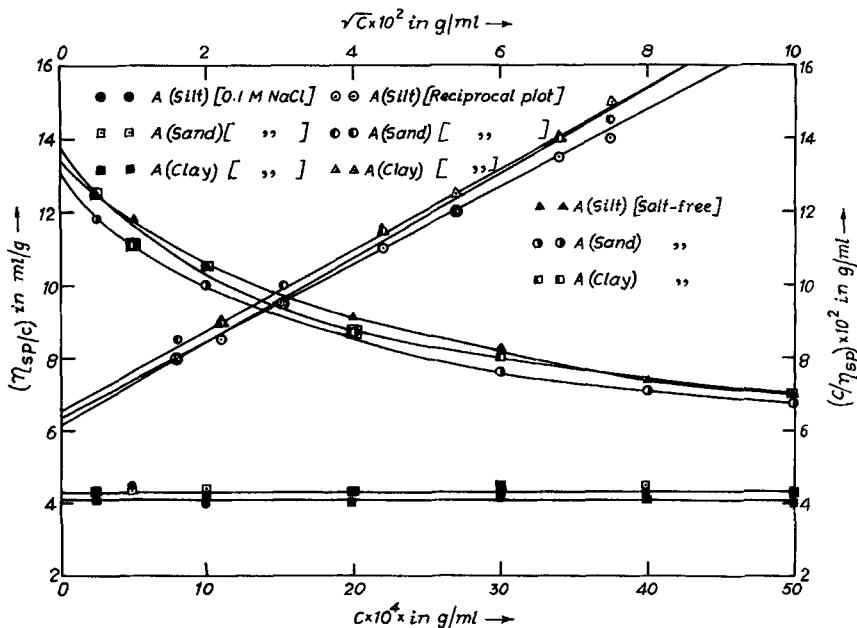


Fig. 1. Typical reduced viscosity vs. concentration curves of hynamelanic acids.

## DISCUSSION

The typical behavior of polyelectrolytes was displayed by all the reduced viscosity-versus-concentration curves. In the absence of salts, as the concentration was gradually decreased, counterions diffused away from the polymer backbone, and the repulsion between similarly charged centers on the polymer chain caused the latter to expand. At infinite dilution, the molecule assumes an extended configuration, accompanied with the maximum possible charge separation.<sup>7</sup> The upward rise of the reduced viscosity-versus-concentration curve in the dilute region was thus caused by intramolecular repulsion. In addition, there is the "electroviscous effect" due to the counterion atmosphere of macroions and the long-range electrostatic coupling between the macromolecules.<sup>8</sup> On the addition of salts, the curves became linear as in the case of a neutral polymer due to complete coiling of the polyelectrolyte molecule. The added electrolyte neutralized the charges on the polymer backbone thereby causing the enormous compression of the hydrodynamic volume. Thus the intrinsic viscosity diminished in the presence of electrolytes from 15.2–33.3 ml/g in aqueous solution to 4.1–12.0 ml/g in salt solution.

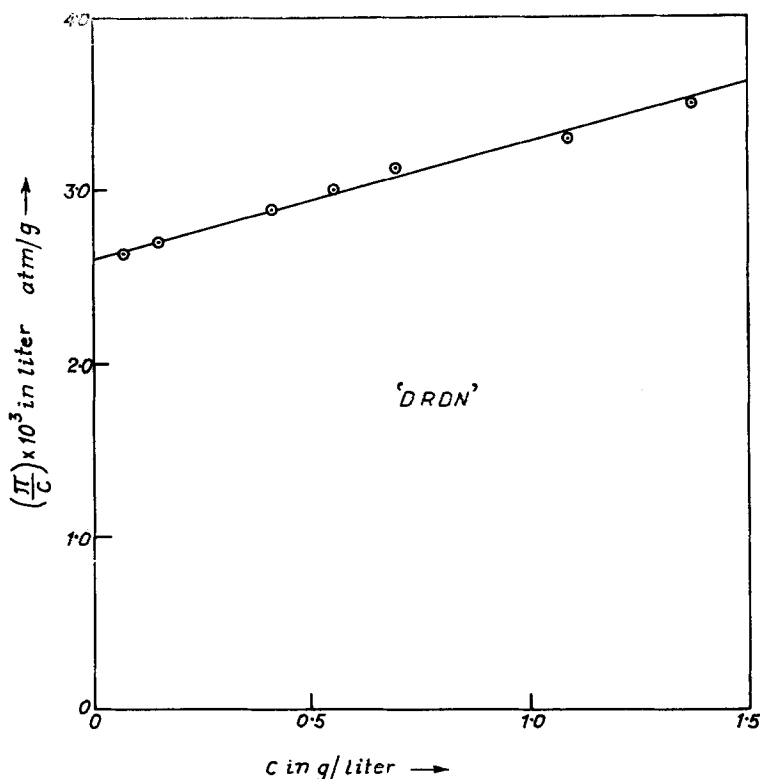


Fig. 2. Typical plot of  $\pi/c$  vs.  $c$  of a natural hymatomelanic acid.

TABLE I

Sample	[ $\eta$ ], ml/g		
	Salt-free medium (Fuoss- Cather's plot <sup>7</sup> )	NaCl medium	
		0.1M	0.0254M
DRDN	27.8	12.0	12.3
PLPR	31.3	7.7	—
JBLP	33.3	10.0	—
BRPR	33.3	8.5	—
A	16.7	4.1	—
AN	16.7	10.0	10.0
A (sand)	15.4	4.2	—
A (silt)	15.9	4.2	—
A (clay)	16.1	4.1	—
C	24.4	6.4	—
CN	18.2	11.0	11.2
C (sand)	20.0	7.1	—
C (silt)	20.4	7.2	—
C (clay)	15.2	7.3	—

TABLE II<sup>a</sup>

Sample	$\bar{M}_n$ (from osmotic pressure measurements)	$(\bar{R}^2)^{1/2}$ , Å [ $\Phi = 2.1 \times 10^{21}$ ]
DRDN	9752	384.9
AN	8108	336.2
CN	8960	363.4

<sup>a</sup> In 0.0254M NaCl medium.

It was to be noted that relative rise or fall in the viscosity of a solution of sodium hymatomelanate was, in fact, much less than that observed in the case of long-chain synthetic polyelectrolytes. This was possibly due to the fact that coiling was restricted to a limited extent by the stereochemical factors of an aromatic chain.

On examining the values of intrinsic viscosities, the conclusion could be drawn that in the absence of neutral electrolytes, natural hymatomelanic acids had higher intrinsic viscosities in comparison to their synthetic counterparts, even when their molecular weights were comparable. This was possibly due to greater flexibility in the molecular chains of natural hymatomelanic acids. With synthetic hymatomelanic acids prepared in the presence of sand/silt or clay as possible catalysts, the intrinsic viscosity values showed no notable change compared to those which were synthesized in the absence of catalysts.

As the samples (sodium hymatomelanate) examined were polyelectrolyte in nature, the osmometric measurements were carried out in a medium of constant sodium chloride concentration. Thus, positive slopes in the figures were obtained. However, several workers<sup>9</sup> have reported that association of humic acid molecules in solution can lead to errors in molecular

weight determinations, since the measurements then correspond, at least in part, to a particle or aggregate weight rather than to a molecular weight.

The values of root-mean-square average end-to-end separations (Table II), as calculated from the conventional Flory-Fox relationship,<sup>10</sup> after complete coiling of the molecules, were found to be comparable among the natural and the synthetic nitrogeneous hymatomelanic acids, provided that the latter were within a comparable range of molecular weights.

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