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Studies of the Precipitation of Humic Acid by Cationic Polyelectrolytes

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In order to elucidate the mechanism of the precipitation of humic acid by two cationic polyelectrolytes, the *n*-butylamine-epichlorohydrin condensation polymer (BECP) and the cyclohexylamine-epichlorohydrin condensation polymer (CECP), electrophoresis and conductometric titration were made in conjunction with precipitation experiments in various concentrations of humic acid with an optimum dosage of cationic polyelectrolyte. The results of these experiments indicated that a cationic polyelectrolyte precipitates the humic acid by combining stoichiometrically with the negatively-charged groups of the humic acid. A possible mechanism for the precipitation was proposed schematically on the basis of the experimental results obtained.

Many previous studies[1-7] of the interaction between surface active agents and proteins have shown that precipitation takes place when they are oppositely charged. Thus, the electrostatic force between their opposite charges is considered to be responsible for the precipitation. However, only a few studies[8,9] have been reported on the interaction between polyelectrolytes with opposite charges.

Previously the present author[10] studied the precipitation of humic acid by cationic polyelectrolytes and found that some cationic polyelectrolytes are excellent precipitants for humic acid, and that the characteristics for the precipitation of humic acid with these cationic polyelectrolytes quite differ from those observed with inorganic salts($BaCl_2$, $Al_2(SO_4)_3$, *etc.*) or with a low-molecular-weight organic cation (*e. g.*, *p*-toluidine hydrochloride).

The present study intends to clarify the mechanism of the precipitation of humic acid with two cationic polyelectrolytes, the *n*-butylamine-epichlorohydrin condensation polymer (BECP) and the cyclohexylamine-epichlorohydrin condensation polymer (CECP).

The relationship between the humic acid concentration and the cationic polyelectrolyte dosage in the precipitation region is investigated in terms of conductometric titration and electrophoresis as well as the transmittance of the test solution.

Experimental

Humic Acid. To 500 g of -149 μ-size Nakayama-lignite, containing 7.92% ash and 10.09% moisture, 1*l* of a 5% aqueous solution of hydrogen peroxide was added; the mixture was then allowed to stand at room temperature (about 20°C). After 24 hr, the lignite was filtered, washed with distilled water, and dried at 107°C for 5 hr. Humic acids prepared by the oxidation of lignite were extracted by the digestion of the oxidized lignite with 5% ammonia water. The aqueous alkali extracts were filtered and boiled in a water bath in order to remove the excess ammonia, and then purified by the use of electrodialysis. The humic acid thus purified was filtered, dried, and dissolved in a sodium hydroxide solution. The aqueous solution of sodium humate of 2 g/*l* in a concentration of pH 7 was prepared as a stock solution and was used throughout the present studies.

The relationship between the concentration and the transmittance of the aqueous solution of sodium humate at pH 7 is illustrated in Fig. 1. The transmittance was measured using a photoelectric colorimeter (Model 7A of the Tokyo Photo-Electric Co., Ltd.) with an 18-mm light path and a 420-mμ filter.

The analyses of purified humic acid are shown in Table 1. The COOH equivalent and the phenolic-OH equivalent of humic acid were determined according to the methods of Higuchi and Shibutani.[11]

Cationic Polymers. As cationic polymers, BECP and CECP were synthesized. The reactions between amines and epichlorohydrin have been studied exten-

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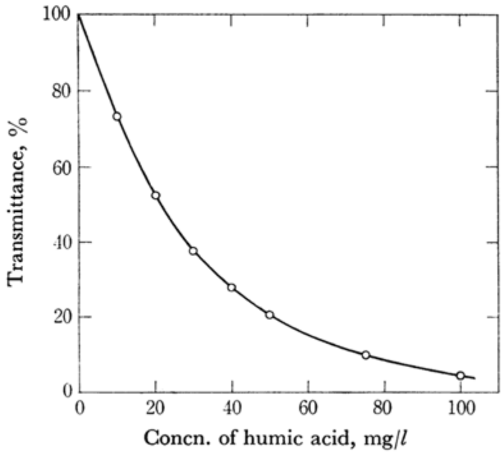
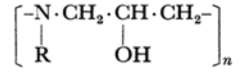


Fig. 1. Relationship between the concentration and the transmittance of the aqueous solution of humic acid.

TABLE 1. ANALYSES OF HUMIC ACID

C %	H %	N %	COOH equiv. g/equiv.	Phenolic-OH eqiuv. g/equiv.	Ash %	Moisture %
58.09	3.05	5.04	288	543	0.93	3.30

sively,[12-18] and it is widely recognized that the structure of monoamine-epichlorohydrin condensation polymers can be represented as follows:



$$\left[\begin{array}{l} -\mathrm{N}\cdot\mathrm{CH_2}\cdot\mathrm{CH}\cdot\mathrm{CH_2}- \\ \ \ | \qquad\qquad\ | \\ \ \mathrm{R} \qquad\qquad \mathrm{OH} \end{array}\right]_n$$

R: butyl or cyclohexyl radical

One mole of epichlorohydrin was poured slowly, with vigorous stirring, into a 200-m*l* flask containing 1 mol of *n*-butylamine or cyclohexylamine and 25 g of water. The mixture was then heated under reflux in a boiling-water bath. After 5 hr of heating, 1 mol of an aqueous solution of sodium hydroxide was added to the mixture, after which heating was continued for an additional 5 hr. The condensation polymer isolated from the reaction mixture by adding sodium hydroxide was washed with hot water, dissolved in benzene, and then washed with water until free from chloride ions; finally, the benzene was evaporated off.

The two condensation polymers obtained were dissolved in a stoichiometric hydrochloric acid solution to a concentration of 50 g/*l*.

The molecular weights of the polymers, determined by means of the cryoscopic method using a benzene solution, were 3080 for BECP and 1720 for CECP.

Nonionic and Anionic Polymers. The following nonionic and anionic polymers were used:

Nonionic polymers: Polyacrylamide, Polyvinylpyrrolidone, Polyvinyl alcohol, Polyethyleneglycol.
Anionic polymers: Polyacrylic acid, Urea-formaldehyde condensation polymer.

The analytical grades of these samples were satisfactory for use as delivered.

Precipitation Procedure. A calculated amount of an aqueous polymer solution was poured into an aqueous solution (20 m*l*) of sodium humate placed in a test tube. Immediately after the addition, the test tube was turned upside-down twenty times at equal time intervals. After it had then been left to stand for 30 min, the solution was filtered through No. 5C filter paper; then the transmittance of the filtrate was measured by the photoelectric colorimeter described above.

The transmittance of the filtrate was utilized as a convenient measure for representing the precipitation of humic acid, because the precipitate, which increases the transmittance of the filtrate, could be removed by filtration.

The dispersing power of cationic polymers for the humic acid precipitated was studied as follows:
An appropriate amount of an aqueous solution of the cationic polymer was added to the humic acid precipitate obtained with an optimum dosage of the cationic polymer. The mixture in a test tube was violently shaken, left to stand for 30 min, and filtered, and the transmittance of the filtrate was measured.

Conductometric Titration. The change in the electric conductivity of the aqueous solution (100 m*l*) of 1 g/*l* sodium humate upon the drop-by-drop addition of a cationic polymer solution (50 g/*l* in concentration) was measured with a conductometric titrator (Model CT-2 of the Shimadzu Seisakusho, Ltd.); at the same time, the precipitation curve of the humic acid - cationic polymer system was determined in a way previously described.

Electrophoresis. A calculated amount of an aqueous polymer solution was poured into an aqueous solution (100 m*l*) of 0.5 g/*l* sodium humate placed in a measuring cylinder. Immediately after the addition, the cylinder was turned upside-down thirty times and then left to stand for 30 min. The electrophoresis of the humic acid in the mixture was qualitatively observed using a U-tube. At the same time, a part of the mixture was filtered, and the transmittance of the filtrate was measured by means of the photoelectric colorimeter described above.

Results and Discussion

The Precipitation of Humic Acid with Water-soluble Polymers. It was found that the precipitation of humic acid occurs only by means of cationic polymers, not by means of nonionic or anionic polymers. The results obtained with two cationic polymers, BECP and CECP, are illustrated in Fig. 2. It is seen that the precipitation of humic acid occurs only within a particular range of concentration of cationic polymers; that

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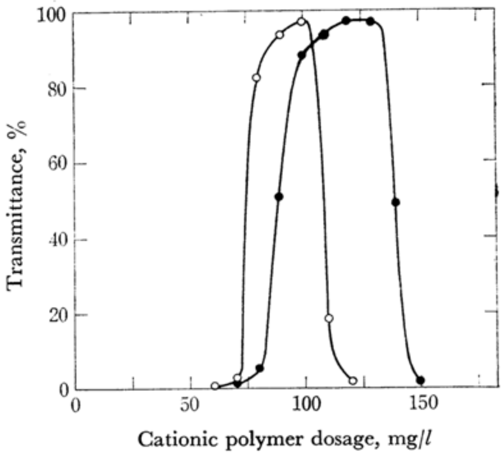

Fig. 2. The precipitation of humic acid by cationic polymers.
Concn. of humic acid: 200 mg/l
—○— BECP, —●— CECP

is, a sharp decrease in precipitating efficiency is observed with excess dosages of cationic polymers. The humic acids once precipitated with cationic polymers were not dispersed by an excess of cationic polymers.

The characteristics of precipitation in the system of humic acid-water soluble polymers are similar to those observed in the system of proteins-surface active agents, except that the proteins precipitated with surface active agents are dispersed by the addition of more of those surface active agents. Also, we know various systems of colloid-water-soluble polymers in which coagulation takes place in a way similar to that observed in the present experiment.

It may be suggested that the precipitation of humic acid with cationic polymers is caused, as in the other examples of colloidal coagulation, by electrostatic interaction between anionic sites of humic acid and cationic sites of cationic polymers. The following experimental results give further support to this idea.

Relation between Initial Humic Acid Concentration and Optimum Cationic Polymer Dosage. The effect of a variation in the cationic polymer dose on the precipitation of a given amount of humic acid was studied at four different humic-acid concentrations (20, 50, 100, and 200 mg/l) at room temperature.

The results obtained are illustrated in Figs. 3 and 4. The abscissa in Figs. 3 and 4 represent the weight-mixing ratio of the cationic polymer to humic acid. The following characteristics may be observed in these figures (Figs. 3 and 4).

(1) Precipitation occurs only over a narrow weight-ratio range of humic acid and cationic polymers, and the range seems to be independent of the initial concentration of humic acid studied; that is, the precipitation of humic acid with a cationic polymer is stoichiometric.

(2) The precipitation of humic acid by BECP occurs in the range of the weight-mixing ratio between 0.35 and 0.55, as is shown in Fig. 3. Since the ratio of the cationic group equivalent (g/equiv.) of BECP to the carboxyl group equivalent (g/equiv.) of humic acid is 0.45, we may infer that the midpoint of the precipitation range corresponds to the point where the number of the cationic group is equal to that of the carboxylic group in the solution. Similar results are observed with CECP. These facts imply that cationic polymers act to precipitate humic acid by combining stoichiometrically with the negatively-charged carboxyl groups of humic acid.

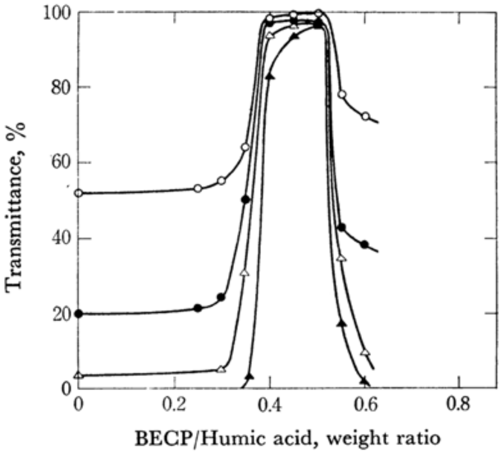

Fig. 3. The precipitation of humic acid by BECP at various concn. of humic acid.
Concn. of humic acid: —○— 20 mg/l, —●— 50 mg/l, —△— 100 mg/l, —▲— 200 mg/l

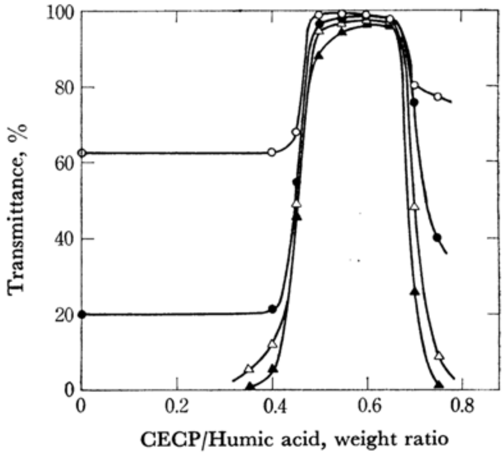

Fig. 4. The precipitation of humic acid by CECP at various concn. of humic acid.
Concn. of humic acid: —○— 20 mg/l, —●— 50 mg/l, —△— 100 mg/l, —▲— 200 mg/l

Conductometric Titration. The results obtained with BECP and with CECP are illustrated in Figs. 5 and 6 respectively. It may be noted in Figs. 5 and 6 that there is a break point in the titration curves, the composition of which nearly coincides with that of the optimum precipitation.

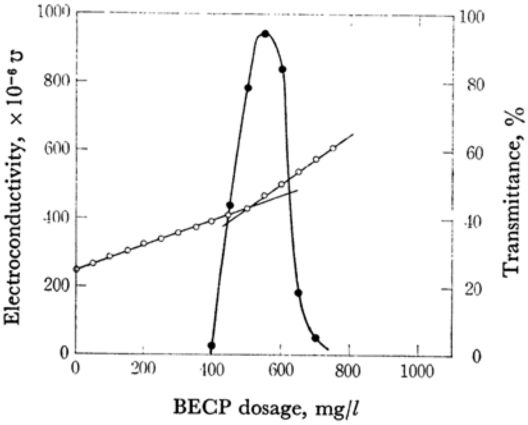

Fig. 5. Relationship between electroconductivity and precipitation in the system humic acid-BECP.
Concn. of humic acid: 1 g/*l*
—○— electroconductivity
—●— transmittance

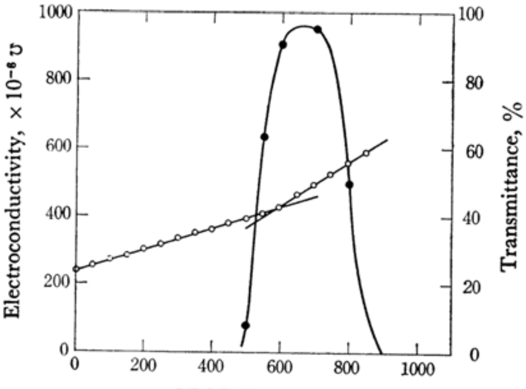

Fig. 6. Relationship between electroconductivity and precipitation in the system humic acid-CECP.

Concn. of humic acid: 1 g/*l*
—○— electroconductivity
—●— transmittance

The results suggest that the precipitation of humic acid occurs as a result of the neutralization of carboxyl groups with a cationic polymer, with a consequent loss of the charge of binding sites.

Electrophoresis. The results obtained with BECP and CECP are summarized in Tables 2 and 3. It is apparent from these tables that the humic acid is negatively charged in the absence of a cationic polymer, that a reversal of charge occurs when the latter reaches a certain concentration, and that optimum precipitation occurs in the narrow range in which the charge of humic acid changes from negative to positive. The decrease in the precipitating efficiency for excess dosages of cationic polymers is caused by a reversal of the charge of humic acid, leading to an increase in the hydrophilic property of humic acid (humic acid-cationic polymer complexes). The phenomena described above in the humic acid-cationic polymer system may be the same as the flocculation-dispersion phenomena in the colloid-polyelectrolyte system, which has opposite charges.

TABLE 2. ELECTROPHORESIS OF HUMIC ACID-BECP MIXTURES

BECP added (mg/*l*)	Precipitation of humic acid	Transmittance of filtrate	Charge on humic acid
0			−
5			−
10			−
15		1.0	−
17.5		3.0	
20	precipitation	41.4	
22.5	precipitation	84.2	
25	precipitation	96.2	
27.5		67.0	
30		5.0	+
32.5		1.0	+
35			+

TABLE 3. ELECTROPHORESIS OF HUMIC ACID-CECP MIXTURES

CECP added (mg/*l*)	Precipitation of humic acid	Transmittance of filtrate	Charge on humic acid
0			−
5			−
10			−
15			−
20		2.9	−
22.5		18.3	
25	precipitation	67.3	
27.5	precipitation	90.0	
30	precipitation	95.3	
32.5	precipitation	96.4	
35		80.0	
37.5		11.2	+
40		3.1	+
45			+

The Mechanism of Precipitation

Humic acids and cationic polymers possess a number of ionized sites on the molecule; for example, the number of cationic groups per molecule

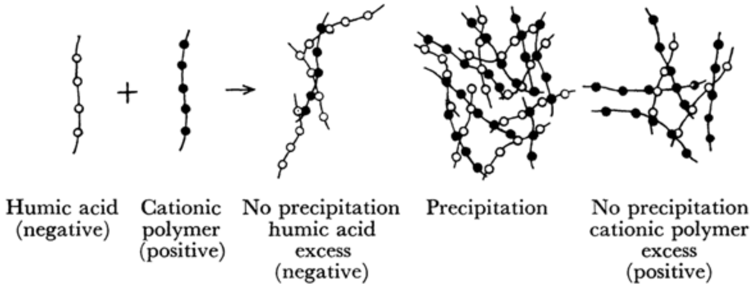

Fig. 7. The precipitation of humic acid by cationic polyelectrolyte.

of BECP is about 24 when the molecular weight is 3080, and that of CECP is about 11 when the molecular weight is 1720. Therefore, it appears to be general true that humic acids may be bridged together by cationic polymers as a result of electrostatic interaction between the carboxyl groups of a humic acid and the cationic groups of a cationic polymer; that is, precipitation is caused by the formation of hydrophobic complexes by a bridging mechanism similar to the polymer-bridging mechanism[19-21] for the flocculation of colloidal suspensions.

Consideration of all of the results obtained in this study leads to the conclusion that the precipitation of humic acid by a cationic polymer is caused by electrostatic and stoichiometric interaction between the anionic sites of humic acid and the cationic sites of the cationic polymer, leading to the formation of salt-like complexes by means of a bridging mechanism. Thus, the precipitation of humic acid by a cationic polymer may be represented schematically as is shown in Fig. 7.

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