Reaction of *N''*-Cyanoguanidine with Formaldehyde (VII). Preparation of New Flocculants for Anionic Colloidal Particles

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Synopsis. New flocculants for anionic colloidal particles were prepared from the reaction of the free bases of *N,N*-(diaminomethylene)urea (DU) and *N,N'*-methylenebis-[*N'*-(diaminomethylene)urea] (Bis-DU) with formaldehyde. These are superior to the resinous product of *N''*-cyanoguanidine with formaldehyde regarding coagulation activity. The gelpermeation chromatograms of these resinous products elucidate that the components of the resin having higher molecular weights as well as the cationic charges play an important role in flocculation.

The resinous products of *N''*-cyanoguanidine (CG) with formaldehyde under acidic conditions are useful as commercial flocculating agents.[1] The reaction of CG with formaldehyde is complicated under acidic conditions, since the simultaneous transform of CG into *N,N*-(diaminomethylene)urea (DU) is accompanied by the hydroxymethylation of CG with formaldehyde and the condensation of hydroxymethylated products with CG, as well as the hydroxymethylation of DU with formaldehyde and the condensation of hydroxymethylated products with DU.[2—6] The flocculation of anionic colloidal particles by the CG-formaldehyde (CG-F) resin has been reported to be caused by a neutralization of the anionic surface charge with cationic DU.[7]

However, our recent report[8] elucidated that neither DU·HCl nor dihydrochlorides of *N,N'*-methylenebis[*N'*-(diaminomethylene)urea] (Bis-DU·2HCl), itself, nor the resinous products of DU·HCl or Bis-DU·2HCl with formaldehyde, are such effective flocculating agents as

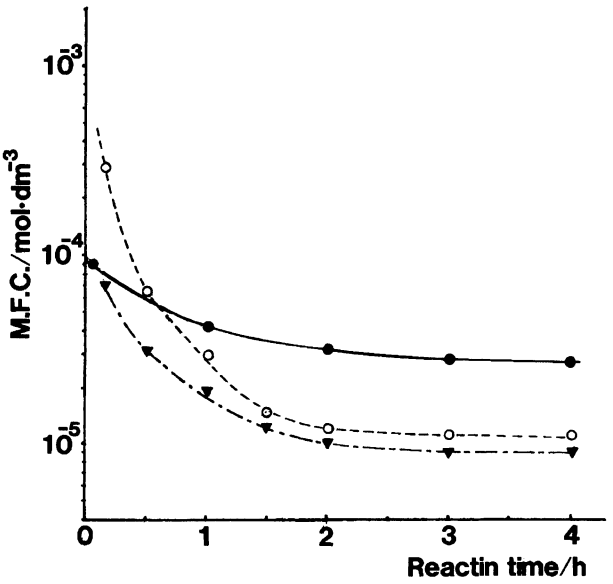

Fig. 1. Improvement of the flocculation efficiency of the resinous products of *N''*-cyanoguanidine (CG), and the free bases of *N,N*-(diaminomethylene)-urea (DU) and *N,N'*-methylenebis[*N'*-(diaminomethylene)urea] (Bis-DU) with formaldehyde with the resinification time. CG-F resin: ●—●, DU-F resin: O---O, Bis-DU-F resin: ▼-·-▼. The flocculation efficiencies of resinous products were measured using Kaolin having an anionic charge. The efficiencies were evaluated in terms of their minimum concentration in which the most rapid flocculation occurred. (M.F.C.: The minimum flocculation concentration (mol dm^{-3})).

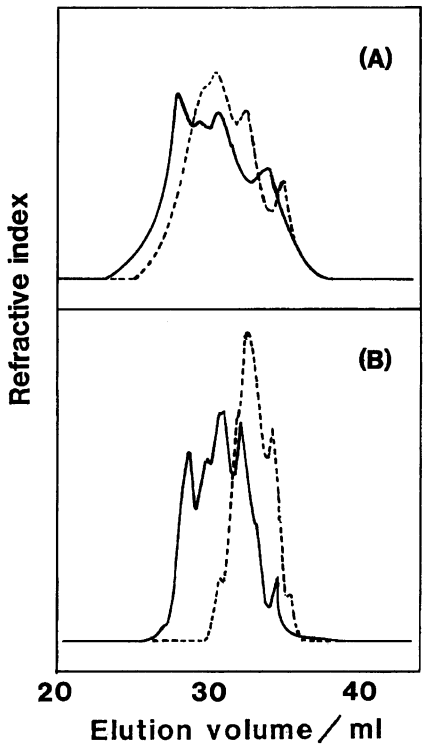

Fig. 2. Gelpermeation chromatograms of the resinous products. Gelpermeation chromatography was carried out on combination columns of TSK gel G2500PW$_{XL}$ and G3000PW$_{XL}$ eluted by a mixed solution of 0.5 mol dm^{-3} acetic acid and 0.5 mol dm^{-3} sodium acetate (1 : 1) at 40 °C. (A): DU-F resin: ---, Bis-DU-F resin: —. (B) was cited from our previous paper,[8] CG-F resin: —, DU·HCl-F resin: ---.

Table 1. Comparison of the Flocculation Efficiency of Several Compounds and Resinous Products: The M.F.C. (the minimum flocculation concentration ($mol\,dm^{-3}$)) is the same in the legend in Fig. 1

Compound or resinous products	log M.F.C.
CG	No flocculation (10^{-6}—10^{-2} $mol\,dm^{-3}$)
DU·HCl	−2.046
Bis-Du·2HCl	−2.081
CG-F resin	−4.569
DU·HCl-F resin	−2.523
Bis-DU·2HCl-F resin	−2.745
DU-F resin	−4.959
Bis-DU-F resin	−5.046

the CG-F resin, and that the flocculation of anionic colloidal particles by the CG-F resin is not explicable in terms of only the electrostatic interaction. This suggested that the components of the resin having higher molecular weights as well as cationic charge play an important role in flocculation.

In order to confirm the flocculation mechanism and to obtain a superior flocculating agent to the CG-F resin, various resinous products were prepared from CG, DU·HCl, Bis-DU·2HCl, and a free base of DU or Bis-DU with formaldehyde by varying such reaction conditions as the feed mole ratios of CG, DU·HCl, Bis-DU·2HCl and free bases of DU, or Bis-DU to formaldehyde, reaction temperatures, pHs, and reaction periods.

Results and Discussion

As shown in Fig. 1, the flocculating activity of resinous products increased as the resinifying reaction proceeded. Table 1 shows the flocculation efficiencies of the related compounds (CG, DU·HCl, and Bis-DU·2HCl) as well as the resinous products of these compounds with formaldehyde according to the value of log M.F.C. (minimum folocculation concentration). The resinous products of free bases of DU and Bis-DU with formaldehyde were superior to those of CG with formaldehyde.

The gelpermeation chromatograms, as shown in Fig. 2, elucidated that the distribution of the molecular weights ranged from 100 to 1800 for DU-formaldehyde (DU-F) resin and from 100 to 2500 for Bis-DU-formaldehyde (Bis-DU-F) resin, which were wider than 150—400 for DU·HCl-formaldehyde (DU·HCl-F) and 200—1200 for CG-F resins, respectively.[8] The components of the resin having higher molecular weights were abundant in the DU-F resin and Bis-DU-F resin as well as in the CG-F resin. These results ascertained our speculation that the components of the resin having higher molecular weights played an important role in flocculation.

Experimental

The Measurement of the Flocculation Efficiency. To carry out a flocculation measurement, 25 ml of 600 $mg\,dm^{-3}$ of Kaolin having anionic charge and a resinous product solution containing 10^{-6}—10^{-2} $mol\,dm^{-3}$ (the final concentration) were introduced to a stoppered test tube; the total volume was then adjusted to 50 ml. The depth of the supernatant over the suspended layer was measured at 10 min intervals for 2 h. The flocculation efficiency of the resinous products was evaluated in terms of their minimum concentration in which the most rapid flocculation occurred.

Gelpermeation Chromatography An aliquot of the resinous products was chromatographycally separated on combination columns comprising TSK gel G2500PW$_{XL}$ and G3000PW$_{XL}$, eluted by a mixed solution of 0.5 $mol\,dm^{-3}$ acetic acid and 0.5 $mol\,dm^{-3}$ sodium acetate (1:1) at 40 °C. The molecular weight of the components of the resinous products were estimated based on calibration curves with polyethylene glycol.

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