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IONIC LINKING OF CARBOXYMETHYLCELLULOSE

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Binding of Al^{3+}, Cu^{2+}, and Co^{2+} ions by carboxymethylcellulose (CMC) macromolecules was studied by potentiometric titration. It has been shown that the metal ions bind electrostatically over a wide pH range. Viscosimetry has found that the effectiveness of intermacromolecular CMC binding increases with increasing initial CMC concentration and in the presence of polybasic acids.

Key words: carboxymethylcellulose, titration, viscosimetry, intramolecular and intermacromolecular linking, metal ions.

Carboxymethylcellulose (CMC) draws much attention in the development of cellulose chemistry. The sodium salt of CMC is widely used in petroleum, textile, food, pharmaceutical, and other technologies primarily because of its good solubility in water and its lack of toxicity [1-5]. Chemical modification of CMC by linking polyfunctional reagents may expand the variety of materials with valuable practical properties.

One possible type of linking reaction is the complexation of CMC macromolecules to polyvalent metal ions [$M^{2+(3+)}$].

We studied the reaction of CMC with Cu^{2+}, Co^{2+}, and Al^{3+} in the presence and absence of polybasic acids (PA).

CMC is a polyacid that contains COOH groups. The content of functional groups is determined by the degree of substitution (DS). These ionizable groups are largely responsible for the behavior of CMC in aqueous solutions. We used a CMC sample with a degree of polymerization (DP) 450 and DS 70.

Adding Al^{3+} ions to an aqueous solution of CMC shifts the potentiometric titration curves as the content of metal ions in solution increases (Fig. 1). Therefore, the part of the ionizable CMC groups that binds to the Al^{3+} is excluded from the acid—base equilibrium. This is indicative of the formation of electrostatic bonds between CMC functional groups and metal ions. The titration results also have shown that complexes form over a wide range of weakly acidic, neutral, and weakly basic media, for example, Cu^{2+} and Co^{2+} simultaneously link two CMC functional groups whereas Al^{3+} links three of them.

Thus, Cu^{2+}, Co^{2+}, and Al^{3+} can be used to link CMC over a wide pH range.

In general, when macromolecules interact with low-molcular-weight polyfunctional reagents intra- or intermacromolecular linking may occur, depending on the experimental conditions, i.e., decreasing the macromolecule size or increasing the polymer molecular weight. In any case, this should have a substantial effect on the hydrodynamic behavior of the solution since it is known that the characteristic viscosity is proportional to the size and molecular weight of the polymer chain [6, 7]:

$$[\eta] = kM^{\alpha}; \ [\eta] = \Phi_0 < h_2 > ^{3/2}M.$$

The simplest and most convenient method for investigating the hydrodynamics of macromolecule solutions is viscosimetry. For dilute CMC solutions (0.156 g/dL) and pH values at which complexes exist, the characteristic viscosity decreases from $[\eta] = 3.8$ dL/g for CMC to $[\eta] = 2.4$ dL/g for the $CMC\cdot Al^{3+}$ complex ($[COOH_{CMC}]/[Al^{3+}] = 5/1$). Increasing the initial CMC concentration to 0.316 g/dL increases the characteristic viscosity of the complex ($[COOH_{CMC}]/[Al^{3+}] = 10/1$) to 4.5 dL/g. Therefore, intramolecular linking by Al^{3+} ions is observed in dilute CMC solutions. This compresses cellulose macromolecules. As the initial CMC concentration increases, primarily intermacromolecular linking occurs with an accompanying increase of molecular weight.

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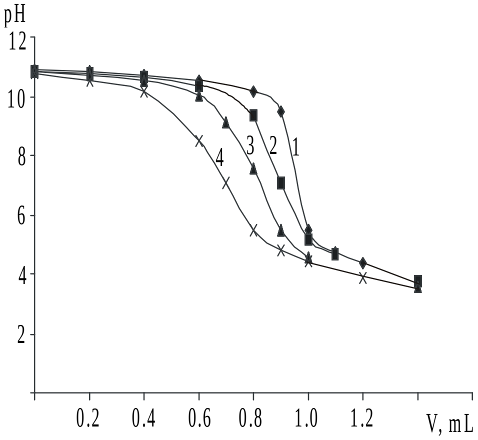

Fig. 1. Potentiometric titration curves of CMC-Al^{3+} at various mole ratios: $[COOH_{CMC}]/[Al^{3+}]$ = 40/1 (2), 20/1 (3), 10/1 (4); CMC (1); $[COOH_{CMC}]$ = 0.01 M.

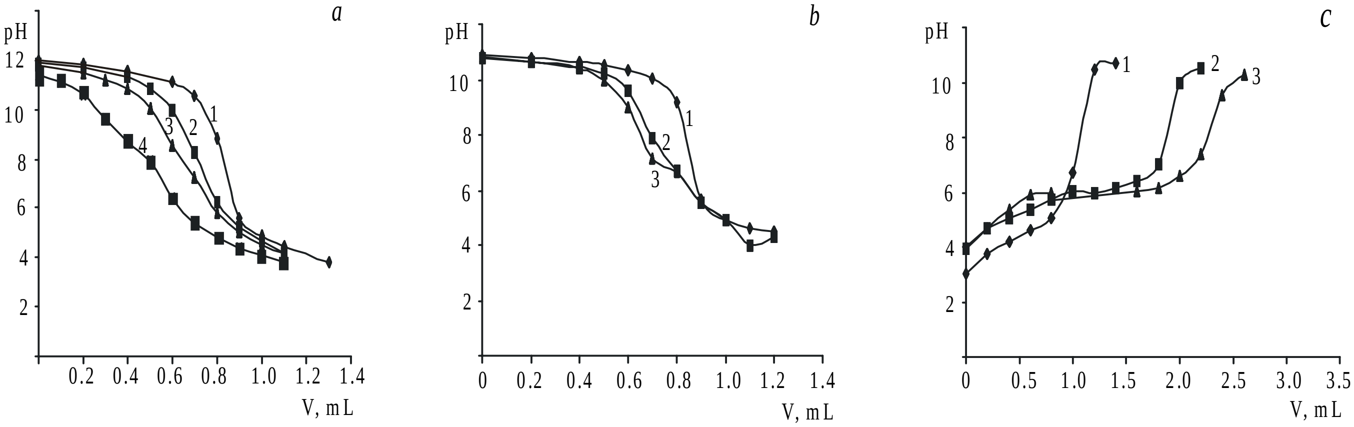

Fig. 2. Potentiometric titration curves: mole ratios: CMC-citric acid—Al^{3+}: $[COOH_{CMC}]/[Al^{3+}]$ = 30/1 (1), 20/1 (3), 10/1 (4); 1 = CMC-citric acid ($[COOH_{CMC}]/[COOH_{acid}]$ = 10/1) (a); CMC-glutaric acid—Cu^{2+}: $[COOH_{CMC}]/[Cu^{2+}]$ = 20/1 (2), 10/1 (3); 1 = CMC-glutaric acid ($[COOH_{CMC}]/[COOH_{glutar}]$ = 10/1) (b); glutaric acid—Cu^{2+} at various mole ratios $[COOH_{glutar}]/[Cu^{2+}]$ = 2/1 (2), 1/1 (3); 1 = glutaric acid (c).

Analogous results were obtained for Cu^{2+} and Co^{2+}.

It should be noted that first opalescence is seen and then a microgel forms with an initial CMC concentration of 0.316 g/dL and $[COOH_{CMC}]/[Al^{3+}]$ = 5/1. Ultracentrifugation has shown that the molecular weight of the sol is 26,000 whereas that of the initial polydisperse CMC is 108,000. This means that the gel fraction in which intermacromolecular linking occurs is formed primarily of the high-molecular-weight part of CMC. Similar results have previously been reported [8-11].

We obtained other parameters in the presence of added PA. Adding succinic, glutaric, or citric acid even to the dilute initial CMC solution (0.156 g/dL) increases the characteristic viscosity of the solution upon linking by Cu^{2+} or Al^{3+}, in contrast with the binary CMC—$M^{2+(3+)}$ systems.

Figures 2a and 2b show potentiometric titration curves for CMC solutions in the presence of PA and metal ions. Here also 2- or 3-functional linking is observed in weakly acidic, neutral, and alkaline media.

The results indicate that the ionic nature of the linking persists and the probability of intermacromolecular CMC linking increases substantially in ternary CMC—PA—$M^{2+(3+)}$ systems.

It can be seen that succinic, glutaric, and citric acids have different effects on the characteristic viscosity. The most effective system for intermacromolecular linking is CMC—citric acid—Al^{3+}, then CMC—glutaric acid—Cu^{2+}, and CMC—succinic acid—Cu^{2+}. It seems that CMC linking occurs through complexes of the type $M^{2+(3+)}COO^{-}–R–COO^{-}M^{2+(3+)}$.

In fact, potentiometry (Fig. 2c) has shown that a complex is formed in the glutaric acid—Cu^{2+} system and H^+ is released into the solution. Analogous results were obtained with succinic and citric acids upon adding Co^{2+} and Al^{3+}. Furthermore, careful analysis of IR spectra and calculation of potentiometric curves for the citric acid—Al^{3+} system [12] also indicates that complexes form at neutral pH values in which one citric acid molecule coordinates three Al^{3+} ions. Consequently, the size of the linker and the effectiveness of intermacromolecular linking increase in the ternary system and the ionic nature of the linking persists. This agrees with the literature [13, 14]. The larger the size and functionality of the linker, the more effective the linking process.

Thus, CMC is linked by Cu^{2+}, Co^{2+}, and Al^{3+} ions through ionic bonds over a wide range of weakly acidic, neutral, and alkaline media.

Intra- or intermacromolecular CMC linking is observed depending on the experimental conditions. As the size of the linker increases with the help of metal complexes with PA, intermacromolecular linking becomes more effective.

EXPERIMENTAL

We used CMC with DP = 450 and DS = 70.

Succinic, glutaric, and citric acids were chemically pure and were used without further purification. $CoCl_2 \cdot 6H_2O$, $CuSO_4 \cdot 5H_2O$, and $Al_2SO_4 \cdot 18H_2O$ were chemically pure and were used without further purification.

Potentiometric titrations were performed with a pH/mv/TEMP Meter P25 (Korea) at $t = 20^\circ C$. The titration in all experiments used HCl (0.1 N) and NaOH (0.2 N).

Ultracentrifugation of the sol-fraction of the $CMC \cdot Al^{3+}$ complex was carried out in a MOM instrument (Hungary) at 50,000 rpm and 25°C. Hydrodynamic studies used a Ubellohde viscosimeter at 25°C. The solvent was NaCl solution (0.2 N) to suppress the polyelectrolyte effect. The flow time for the solvent was $\tau_0 = 102.0$ s.

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