Polarographic Investigation of Copper(II)-Poly(*α*, L-Glutamic Acid) Complex in the Helix-Coil Transition Region

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We wish to report results of a polarographic study of the aqueous solution of cupric chloride in the presence of poly (α,L-glutamic acid) in the pH range 3.0—6.0 where the polymer alone is known to undergo conformational transitions. The purpose of this investigation is to obtain electrochemical data for a better understanding of the mechanism of the pH induced helix-coil transition of synthetic polyamino acids with ionizable side chains. This can be achieved by adding, as a structural probe, a small amount of any polarographically reducible metallic ion which can form a stable complex with polymer but does not perturb polymer conformation.

The cupric ion, which is known to bind to poly (α, L-glutamic acid),[1] could be reduced at the dropping mercury electrode either in the presence or absence of the polymer in the pH range examined. The variation of the limiting current of Cu(II) in the Cu(II)-polymer solution with pH (i_l-pH curve) was affected most by the nature of supporting electrolyte. The paralellism between the i_l-pH curve and helix-coil transition curves obtained with other methods such as viscosity[2] and optical rotation[2] became apparent only when the concentration of the supporting electrolyte so decreased that it was comparable with the concentration of the polymer. The polarographic limiting currents were determined in two extreme sets of supporting electrolytes. The concentration of cupric ions was 1×10^{-4} M and the mean residue weight concentration of the polymer was 1.6×10^{-3} M, the ratio of the monomer unit of the polymer to cupric ion being 16 in the Cu(II)-polymer solution. The limiting current of Cu(II) could be attributed to the diffusion-controlled current (i_d)[3] both in the presence and absence of the polymer in the solution containing either of the two supporting electrolytes, since a strict linear relationship, which could be extrapolated to intercept the origin, was obtained between the observed current and the product of $m^{2/3}\cdot t^{1/6}$, where m is the flow rate of mercury and t the drop time. This relation also held for the Cu(II)-polymer solution at pH 3.5 or 6.5, where the complex is in helical or random-coil conformation, thus ruling out the contribution of migration current to i_l.

Without the polymer, Cu(II) was reduced at a half-wave potential $E_{1/2}$=0.05 V *vs.* SCE in the entire pH region and the diffusion current did not significantly decrease at pH 3.0—6.0 in either of the two supporting electrolytes. In the presence of the polymer, however, Cu(II) was reduced at $E_{1/2}$=0.00 V *vs.* SCE, while the diffusion current sharply decreased with increase in pH between 4 and 5. In Fig. 1 the data are expressed in terms of the ratio of diffusion current of Cu(II) with the polymer to that without it, $(i_d)_p/(i_d)_o$, in each supporting electrolyte system. Based on the fact that the electrode mechanism of the reduction of Cu(II) is invariant, the ratio of the two diffusion constant (D_p/D_o) was also calculated with the aid of Ilkovic's equation and is plotted in Fig. 1. On the assumption that two electrons are transferred from each Cu(II), the diffusion constants at pH 3.8 and 5.0 were calculated to be 6.3×10^{-6} and 0.97×10^{-6} (cm²/sec), respectively, for the Cu(II)-polymer solution in 1.5×10^{-3} M NaCl at 25°C.

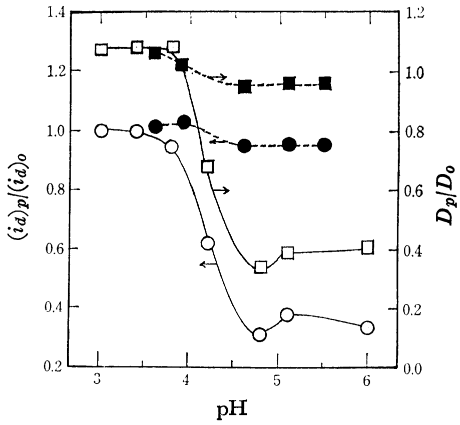

Fig. 1. The pH dependence of polarographic diffusion currents and diffusion constants of the Cu(II)-poly(α,L-glutamic acid). ●,■: $(i_d)_p/(i_d)_o$ and D_p/D_o in 0.2 M acetic acid-sodium acetate buffer, ○,□: $(i_d)_p/(i_d)_o$ and D_p/D_o in 1.5×10^{-3} M sodium chloride. Polarographic currents were memeasured manually on a Yanagimoto Model P-8 polarograph.

The curves in acetate buffer indicate that cupric ions interact with acetate ions more strongly than with ionized polymer molecules, or that the electrode process is independent of the conformation of Cu(II)-polymer complex. On the other hand, the interaction between Cu(II) and polymer primarily controls the electrode reduction process in low sodium chloride concentration. The decrease in $(i_d)_p/(i_d)_o$ values at higher pH may be assumed to result from the formation of both electrostatic ion-pairs and inter- and/or intramolecular chelate complexes with the amide and carboxyl groups of the polymer. In conclusion, polarographic methods can be utilized in elucidating the mechanism of the helix-coil transition of ionizable polyamino acids.

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