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Electrode Reactions of Several Transition Metal Ions in Aqueous Polyelectrolyte Solutions as Studied by DC and Fourier Transform Polarography

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Synopsis. The kinetic parameters, k_s for several metal ions are decreased down to 1/10—1/50 in the presence of sodium polyacrylate, although the diffusion of metal ions in the same system differs little with and without sodium polyaclylate.

The electrochemical behavior of proteins and macromolecules has been gaining popularity in recent years.[1,2] In a preceding paper,[3] the diffusion coefficient of transition metal ions in polyelectrolyte solutions has been studied polarographically. However, due to the complexity of overall reactions involved, we could not discuss the following two effects separately; i) adsorption of polyelectrolytes on the surface of the mercury electrode, ii) complex formation of metal ions with polyelectrolytes.

In the present study, the effect of polyacrylate on the reduction process of transition metal ions at the surface of the dropping mercury electrode (DME) will be studied briefly in terms of the adsorption, complex formation with metal ions, and the influence on the kinetic parameters of metal ions.

Sodium polyacrylate (M.W. 2500—7500) purchased from WAKO Chemicals Co. was purified as reported previously.[3] In all cases, 1 M $NaClO_4$ was added to 5 mM polyacrylate aqueous solution in order to make the IR drop of the solution minimum. A saturated calomel electrode (SCE) was used as the reference electrode. The flow rate of mercury was 7.52 mg/s at a mercury column height of 40 cm in 1 M $NaClO_4$ solution at an open circuit. All measurements were performed at (25.0±0.5) °C. The standard rate constant (k_s) and the transfer coefficient (α) were determined using FT polarography, where details of the analysis were also described in the previous paper.[4] Two kinds of the AC potentials with the frequencies of 55.8 and 173.6 Hz and an amplitude (ΔE) of 5 mV were used. Simulations for obtaining k_s and α were performed on a HITAC 8700/8800 system at the Computer Center, The University of Tokyo, using the FORTRAN program written and kindly given by Prof. D. E. Smith.

Adsorption of Polyelectrolyte on DME. From the electrocapillary curves for 1 M $NaClO_4$ solutions with and without sodium polyacrylate, poly(acrylic acid) adsorbs on the DME only when the concentration of proton reaches a value of *ca.* 10 mM. The differential capacity of the interface with and without poly(acrylic acid) were obtained from the fundamental AC current measured by the Fourier Transform AC polarography using the equation

$$C = \frac{I}{f\Delta E},$$

where ΔE is the amplitude of the applied AC voltage, I the resulting fundamental AC current and f the frequency in Hz. The great decrease in the value of capacitance was observed in the presence of polyacrylic acid. This is interpretable in terms of the decrease in the double layer charge due to the adsorption of neutral poly(acrylic acid). No frequency dependence was observed from 55.8 to 173.6 Hz. This result implies that the adsorption equilibrium is fast enough as compared with the time scale of 0.02—0.006 s.

Diffusion Current. As shown in Table 1, the magnitude of diffusion currents of metal ions in 5 mM sodium polyacrylate is dependent on the proton ion concentration of the sample solution. When the value of pH decreases, the magnitude of diffusion currents increases to reach the value in 1 M $NaClO_4$ solution without sodium polyacrylate.

Table 1. pH dependence of diffusion currents for metal ions with and without sodium polyacrylate
(Diffusion current μA)

HNO_3 added	No polyacrylate		5 mM polyacrylate		
	0 mM	0 mM	1 mM	3 mM	10 mM
$MnCl_2$	8.2	6.3	7.1	8.3	N[a]
$CoCl_2$	9.4	5.3	6.3	8.1	N
$ZnSO_4$	9.6	N	N	N	9.3
$Pb(NO_3)_2$	11.0	N	N	N	10.8
$Cd(NO_3)_2$	9.8	N	N	N	9.6

a) N: The diffusion currents could not be measured due to the interference of the hydrogen wave and precipitation of hydroxides for Mn(II), Co(II) and Zn(II), Pb(II), Cd(II), respectively.

Possible mechanisms for change in diffusion currents in the presence of sodium polyacrylate are: i) decrease in diffusion coefficient of metal ions due to the complex formation with polyacrylate and/or ii) blocking effect of poly(acrylic acid) adsorbed layer on the diffusion of metal ions. Of these two, the mechanism ii) should be pronounced when the pH values decrease, because the formation of the adsorbed blocking layer, if any, is enhanced in lower pH ranges. However, the observed phenomenon is opposite to expectation from the mechanism ii). From these results, it is concluded that the increase in diffusion currents of metal ions with lower pH is explained in terms of the increase in the diffusion constant through dissociation

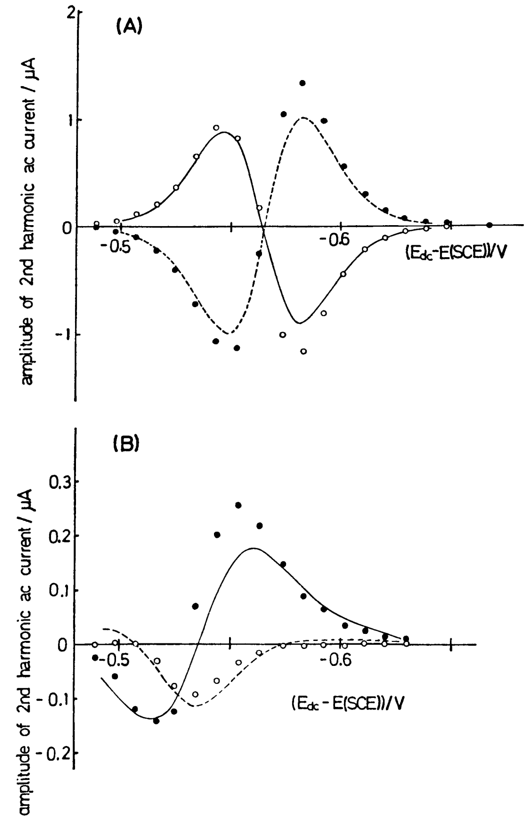

Fig. 1. The second harmonic AC polarogram of cadmium(II) ion with and without sodium polyacryate. ○: In-phase component, ●: quadrature component 2 mM Cd(II) and 1 M $NaClO_4$, (A) no sodium polyacrylate. (B) 5 mM sodium polyacrylate and 10 mM HNO_3.

of polyacrylate ligand from metal ions in acidic media.

Kinetics. Although the adsorbed layer of polyacrylic acid on the DME did not affect the diffusion current of metal ions at low pH regions (see preceding section), the kinetic parameters for the electrode reaction of these metal ions were greatly influenced by this adsorption layer. The kinetic parameters of electrode reactions with and without sodium polyacrylate was obtained through the second harmonic AC polarogram. Typical examples of the second harmonic polarogram for Cd(II) ion with and without sodium polyacrylate in acidic media are shown in Fig. 1, where the computer simulation were performed on these curves using the theoretical equation for the quasi-reversible 2nd harmonic polarogram.[7] The second harmonic polarograms with and without sodium polyacrylate differ appreciably each other.

TABLE 2. KINETIC PARAMETERS (k_s, α) WITH AND WITHOUT SODIUM POLYACRYLATE

		α	k_s[c]/cm s^{-1}
$CdSO_4$	a)	0.15[d]	0.45[d]
	b)	0.30±0.02	0.0083±0.0005
$Pb(NO_3)_2$	a)	0.61[e]	10.2[e]
	b)	0.70±0.06	0.19±0.08
$Zn(NO_3)_2$	a)	0.30±0.04	$(3.0\pm1.0)\times10^{-3}$
	b)		$(4\pm2)\times10^{-4}$ [f]

a) No sodium polyacrylate. b) 5 mM sodium polyacrylate, $[HNO_3]=10$ mM. c) Observed rate constant. d) Values from Ref. 5. e) Values from Ref. 6. f) A well-defined second harmonic polarogram were not obtained. Therefore, k_s values roughly estimated from DC polarography.

The kinetic parameters obtained are summarized in Table 2. It is seen that in the presence of 5 mM polyacrylic acid, the value of k_s decreases down to 1/10—1/50 of those obtained without poly(acrylic acid). The shift of half-wave potential and the change in the slope for log $(i/(i_d-i))$ *vs.* E relation were obtained upon the addition of poly(acrylic acid). It is interesting to note that even if the value of kinetic parameters for Pb(II) and Cd(II) decreased upon adding poly(acrylic acid), the DC polarographic parameters such as $\Delta E_{1/2}$ and log $(i/(i_d-i))$ *vs.* E plot for those ions with and without sodium polyacrylate exhibit little change, indicating the electrode reaction for those system is still fast enough as compared with the DC polarographic time scale ($<5\times10^{-4}$ cm s^{-1}).

In conclusion, an electron transfer from the electrode to the metal ions becomes restricted appreciably in the presence of sodium polyacrylate, although the diffusion of metal ions in the same system differs little with and without sodium polyacrylate.

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