

## Influence of Adsorbed Positively Charged Polyelectrolytes on Polarographic Currents of Cationic Depolarizers. II

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The effect of adsorbed polyelectrolytes on diffusion currents and on current *vs.* time curves, during the lifetime of a single mercury droplet, was measured at selected constant potentials. Cationic depolarizers such as  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  and basic polyelectrolytes, for example, polyvinylpyridine and bovine serum albumin in acid solutions, were employed in these experiments. Positively charged polymers adsorbed on the mercury surface form a barrier against the transport of charges carried by cationic depolarizers and thus impede the diffusion current. The obstruction effect of the polymeric barrier can be suppressed by reducing, or even more by inverting, the charge of either the polyelectrolyte or the depolarizer. The polyelectrolyte charge was altered by varying the pH of the solution and the charge of the depolarizers by complexing anions. The impeding effect of the polymer charge in the surface was also controlled by screening with the aid of different concentrations of supporting electrolyte. The salt concentration affects the distribution coefficient of the depolarizer between the aqueous solution and the surface phase.

### Introduction

The influence of adsorbed surface-active materials on polarographic waves and currents has been investigated by many authors.<sup>1-3</sup> Some investigators have concentrated on the influence of the adsorbed materials on the current-voltage curves, considering the suppression of the diffusion currents, the changes in the wave shapes, and the shift in the half-wave potentials. Others have studied the effect of the kinetics of adsorption on the polarographic currents, by measuring the variation in current with time on single drops and at fixed potentials.<sup>4</sup> The problem has also been treated theoretically by solving the differential equations for the simultaneous diffusion of the surface-active materials and the depolarizers.<sup>5,6</sup> The structure of the adsorbed layer and its free energy of adsorption have a pronounced effect on the diffusion current through it; thus, a great deal can be learned from the diffusion current about the structure of the layer and the interacting forces.

One of the principal aims of the present study is the elucidation of the structure and conformation of adsorbed polyelectrolytes. It is considered that valuable information can be obtained by the use of polaro-

graphic techniques, especially the measurement of current-time curves, which offer detailed information on the structure of partly saturated as well as fully saturated adsorbed monolayers of polyelectrolytes.

### Experimental

The experiments were performed using a Shimadzu polarograph (Type RP-2). The surface of the mercury drop was polarized against a mercury pool, but the potentials were recorded relative to a saturated calomel electrode. The capillary was of marine barometer type, supplied with the instrument. A small pressure head was used in order to get long drop times, of the order of 10 to 15 sec. The curves were recorded without damping. Since the polarograms were taken with long drop times and at high chart

- (1) C. Tanford, *J. Am. Chem. Soc.*, **74**, 211 (1952).
- (2) C. N. Reilly and W. Stumm, *Progr. Polaro.*, **1**, 81 (1962).
- (3) E. Jacobsen and G. Kalland, *Anal. Chim. Acta*, **30**, 240 (1964).
- (4) J. Kuta and I. Smoler, *Progr. Polaro.*, **1**, 43 (1962).
- (5) J. Weber, J. Koutecky, and J. Koryta, *Z. Elektrochem.*, **63**, 583 (1959).
- (6) P. Delahay and I. Trachtenberg, *J. Am. Chem. Soc.*, **79**, 2355 (1957); **80**, 2095 (1958).

speed, they also have the characteristics of current-time curves. Indeed, since the voltage change was very small (between 20 and 30 mv.) and the voltage dependence of the transfer constant also quite small, the curves are essentially similar to those obtained by Schmid and Reilly<sup>7</sup> and Kuta and Smoler,<sup>8</sup> who measured true current-time ( $i-t$ ) curves, and they are so designated later. They are indistinguishable from the ( $i-t$ ) curves measured at constant potential. The ( $i-t$ ) curves were recorded *via* a suitable amplifier on a Tektronix 5B 1A oscilloscope. In the type of capillary used, the mercury drops are formed in an environment which allows concentration polarization. However, in the presence of surfactants the concentration polarization is usually repressed, so that the difference between curves for first and subsequent drops disappears.

All materials used were of analytical grade. Polymers were prepared as previously reported.<sup>9,10</sup> Doubly distilled water was used for preparing the solutions for polarography. The concentration of the depolarizers was about  $10^{-3}$  M, while that of the supporting electrolyte varied between 0.05 and 1 N. The concentrations of polyelectrolytes were chosen so that a fully saturated monolayer was obtained within 1–10 sec.

Crystalline bovine serum albumin was employed (Armour Lot T68204).

## Results

**Poly-2-vinylpyridine (2PVP).** 2PVP at a monomer concentration of  $10^{-3}$  M was added to  $10^{-3}$  M Cd-(NO<sub>3</sub>)<sub>2</sub> solution in 0.2 M KNO<sub>3</sub> and 0.1 M HNO<sub>3</sub>. At drop times of 10 to 14 sec., a splitting of the current diagram for a single drop was observed (Figure 1). The discontinuities indicate the start and termination of the drop. An initial rise in current can be seen, followed by a fall and a subsequent rise once more. The ratio of the heights of the first and second rise depends on the voltage. The whole polarographic wave is depressed in comparison with the blank containing depolarizer and supporting electrolyte only. The time taken for the current to reach its minimum value is independent of voltage. At a concentration of  $2 \times 10^{-4}$  N 2PVP and drop times of less than 15 sec., the polymer has no influence on the polarogram. At a polymer concentration of  $5 \times 10^{-4}$  N a slight flattening of the current-time wave is just discernible. Above this value and up to about  $2 \times 10^{-3}$  N the split illustrated in Figure 1 occurs. At still higher concentrations only the current rise through the surface fully covered by PVP is observed.

Above these concentrations there is an over-all suppression of the diffusion current which is independent

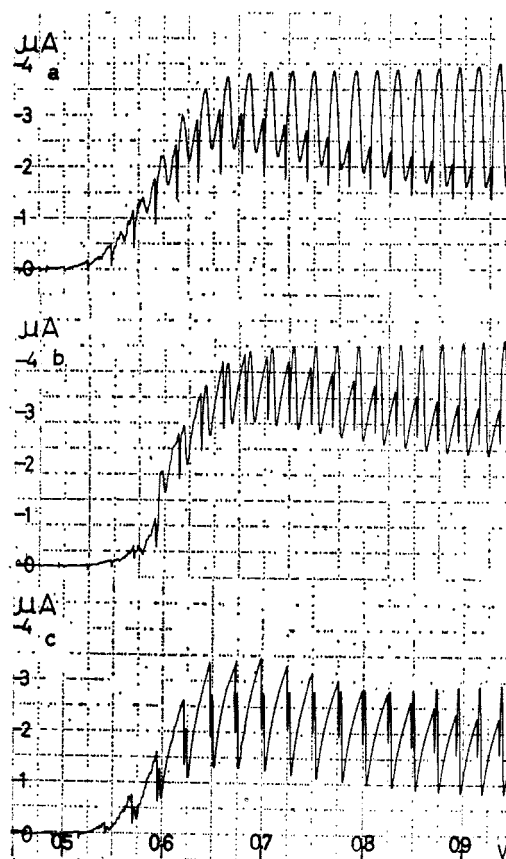


Figure 1. Polarograms of Cd<sup>2+</sup> in the presence of 2PVP: (a) 2PVP,  $8 \times 10^{-4}$  N; HNO<sub>3</sub>, 0.055 N; KNO<sub>3</sub>, 0.3 N; Cd<sup>2+</sup>,  $10^{-3}$  M. (b) 2PVP,  $10^{-3}$  N; HNO<sub>3</sub>, 0.06 N; KNO<sub>3</sub>, 0.3 N; Cd<sup>2+</sup>,  $10^{-3}$  M. (c) 2PVP,  $1.5 \times 10^{-3}$  N; HNO<sub>3</sub>, 0.065 N; KNO<sub>3</sub>, 0.3 N; Cd<sup>2+</sup>,  $10^{-3}$  M.

of the polymer concentration. The split-wave character of the current-time curves does not depend on the Cd<sup>2+</sup> concentration. The addition of the polymer caused no shift in the half-wave potential. If the adsorption is diffusion controlled, it obeys the relation  $Ct^{1/2} = \text{constant}$ , where  $C$  is the concentration of the surfactant and  $t$  the time from the beginning of growth of the drop till the current reaches its minimum. Table I shows that this relation holds true within the experimental error of the measurements.

These phenomena were not observed in CdCl<sub>2</sub> solutions as Cd<sup>2+</sup> gives with Cl<sup>-</sup> neutral and negative complexes.<sup>1</sup> CuSO<sub>4</sub> in 0.2 N KNO<sub>3</sub> and 0.1 N HNO<sub>3</sub> as supporting electrolyte gave results similar to those obtained with Cd(NO<sub>3</sub>)<sub>2</sub>. In the voltage range 0 to

(7) R. W. Schmid and C. N. Reilly, *J. Am. Chem. Soc.* **80**, 2087 (1958).

(8) J. Kuta and I. Smoler, *Z. Elektrochem.*, **64**, 285 (1960).

(9) I. R. Miller and D. C. Grahame, *J. Colloid Sci.*, **16**, 23 (1961).

(10) I. R. Miller and A. Katchalsky, *Proc. Intern. Congr. Surface Activity*, 2nd, London, 1957, 159 (1957).

**Table I:** Concentration-Time Relations at Saturation Point

$C, N$	$t, \text{sec.}$	$Ct^{1/2} \times 10^2$
$2 \times 10^{-3}$	1.5	2.45
$1.2 \times 10^{-3}$	3.75	2.32
$0.9 \times 10^{-3}$	8.25	2.58

-0.5 v., the first current rise is discernible only as a shoulder, and the current minimum is barely seen (see Figure 2a), indicating that in this voltage region the adsorbed 2PVP molecules do not constitute a very strong barrier to the approach of the  $\text{Cu}^{2+}$  to the mercury surface. This finding is in keeping with the only relatively small lowering of surface tension by the adsorbed 2PVP at potentials more positive than -0.3 v. with respect to s.c.e., shown in electrocapillary curves obtained in the presence of 2PVP.<sup>9</sup>

The polarographic waves of  $\text{Pb}(\text{NO}_3)_2$  and  $\text{Fe}(\text{NO}_3)_3$  were not influenced by the presence of the polymer.

**Poly-4-vinylpyridine (4PVP).** The phenomenon of the double-peaked current-time polarogram was also observed with 4PVP. In this case, at  $10^{-3} M$  monomer concentration, the second peak was the dominant one. The ratio between the two peaks was much less dependent on voltage than in the case of 2PVP (Figure 3). From the differential capacity curves measured by Miller and Grahame<sup>9</sup> for 4PVP, it is seen that, while this substance is adsorbed at a more positive potential than 2PVP, the adsorption is weaker because of its more polar character. This is in keeping with the greater flexibility of 4PVP, which can be oriented on the positively polarized mercury surface with the polar groups toward the water and the hydrophobic groups toward the mercury. At negative polarization, the orientation of the polar groups can be reversed.

In aqueous solutions, 4PVP serves as a smaller barrier to the depolarization of cations than 2PVP, probably because of the larger average distances between the positive polymeric charges.  $\text{Cu}^{2+}$  as depolarizer gave at identical potentials the same results as did  $\text{Cd}^{2+}$  (Figure 2b).

**Copolymers.** A copolymer consisting of 40% 4-VP (4-vinylpyridine) and 60% MA (methacrylic acid) was also investigated. The influence of the copolymer on the polarograms of  $\text{Cd}^{2+}$  in nitrate solution was measured at high and low pH. At pH 1 and  $10^{-3} N$  copolymer concentration, the same slight differentiation of the current-time curves into two peaks as obtained with 4PVP was observed. There was also a diffusion current depression. At a slightly higher pH (pH 2) the differentiation into two peaks became less distinct.

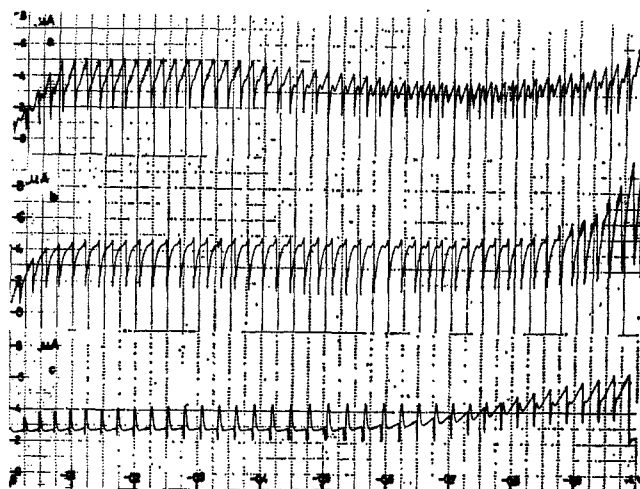


Figure 2. Polarograms of  $\text{Cu}^{2+}$  in the presence of 2PVP, 4PVP, and BSA: (a) 2PVP,  $10^{-3} N$ ;  $\text{HNO}_3$ , 0.1  $N$ ;  $\text{KNO}_3$ , 0.2  $N$ ;  $\text{Cu}^{2+}$ ,  $9 \times 10^{-4} M$ . (b) 4PVP,  $5 \times 10^{-4} N$ ;  $\text{HNO}_3$ , 0.1  $N$ ;  $\text{KNO}_3$ , 0.2  $N$ ;  $\text{Cu}^{2+}$ ,  $10^{-3} M$ . (c) BSA, 0.015%;  $\text{HNO}_3$ , 0.1  $N$ ;  $\text{KNO}_3$ , 0.2  $N$ ;  $\text{Cu}^{2+}$ ,  $9 \times 10^{-4} M$ .

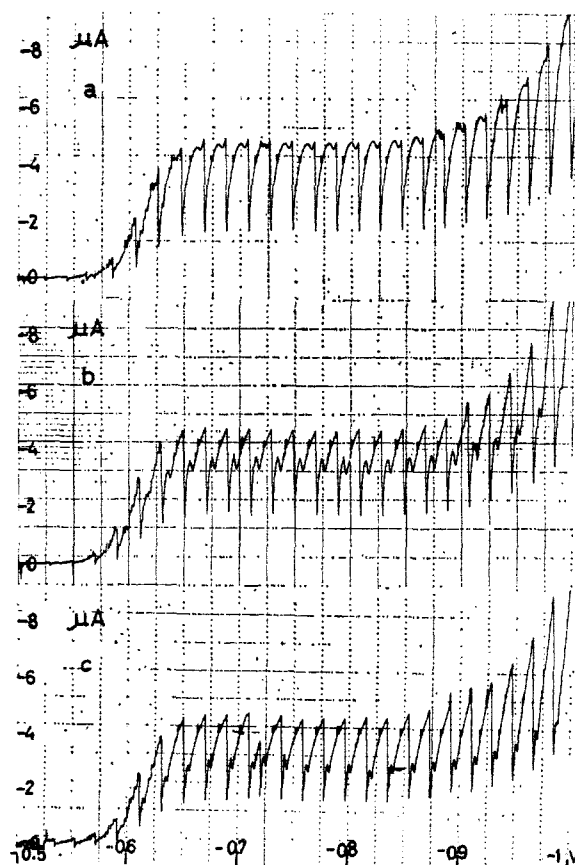


Figure 3. Polarograms of  $\text{Cd}^{2+}$  in the presence of 4PVP, 0.1  $N$   $\text{HNO}_3$  and 0.2  $N$   $\text{KNO}_3$  as supporting electrolyte: (a) 4PVP,  $5 \times 10^{-4} N$ ;  $\text{Cd}^{2+}$ ,  $9.5 \times 10^{-4} M$ . (b) 4PVP,  $7.5 \times 10^{-4} N$ ;  $\text{Cd}^{2+}$ ,  $9.2 \times 10^{-4} M$ . (c) 4PVP,  $1.10 \times 10^{-3} N$ ;  $\text{Cd}^{2+}$ ,  $9 \times 10^{-4} M$ .

No influence of the negatively charged copolymer on the current-time curves in the presence of  $\text{Cu}^{2+}$  or  $\text{Cd}^{2+}$  could be observed at pH 7.

**Effect of Salt Concentration.** The results indicate quite clearly that it is the positive charge of the adsorbed polyelectrolytes rather than the steric hindrance which is responsible for barring the approach of the positively charged depolarizer to the surface. The results of the experiments carried out in the presence of different concentrations of supporting electrolyte further support this conclusion. As shown previously<sup>11</sup> and as is also evident from results not yet published, increase in salt concentration enhances the adsorbability of polyelectrolyte on the polarized mercury surface. If the steric hindrance were responsible for the barrier to the charge transfer across the interface, increase in salt concentration would cause the diffusion current to fall. If, however, access of the positively charged depolarizer were barred by the screen of positive polymeric charges, increase in salt concentration would have the opposite effect. It can be seen from Figures 4 and 5 that the second alternative is the prime factor in the effect of the salt concentration on the diffusion current.

In this respect 2PVP (*i-t* curve Figure 4) and 4PVP (*i-t* curve Figure 5) behave similarly although there is a quantitative difference in their efficacy as a barrier to charge transfer.

**Bovine Serum Albumin.** Tanford<sup>1</sup> investigated the influence of adsorbed acid bovine serum albumin (BSA) on the polarograms of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cd}^{2+}$ . He used a BSA concentration of 1.23%. The curves obtained with  $\text{Cu}^{2+}$  in  $\text{NO}_3^-$  were irreversible. In KCl, no influence of BSA was observed on the waves of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  because of complex formation. It was therefore interesting to investigate the influence of acid BSA at lower concentrations. With a 0.015% solution of BSA in  $10^{-3} M \text{ Cu}^{2+}$ ,  $0.2 M \text{ KNO}_3$ , and  $0.1 M \text{ HNO}_3$ , a general depression of the diffusion current was observed. The current-time curve showed that up to  $-0.6$  v. relative to s.c.e., there was only a slight rise in current after full coverage of the surface by BSA (Figure 2c). At this potential ( $0.6$  v.) the slope of the current-time curve section, corresponding to the fully covered surface, begins to increase with increasing potential, indicating a rising tendency of the BSA to desorb. In a 0.15% BSA solution, practically complete suppression of the diffusion current was observed between  $0$  and  $-0.7$  v.; the current begins to rise after  $-0.7$  v. Only one peak was observed in the current-time curve.

With  $\text{Cd}(\text{NO}_3)_2$  as depolarizer the depression of the diffusion current and of the second peak in the current-

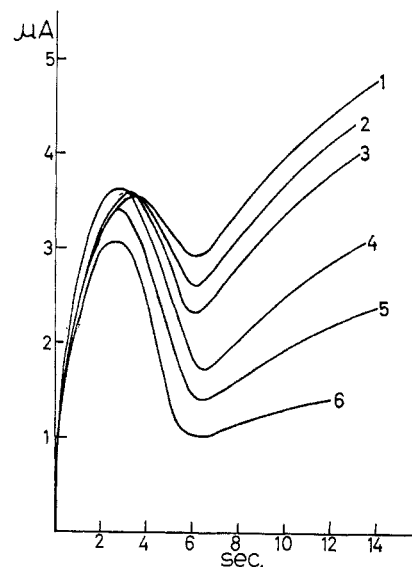


Figure 4. Current-time curves of 2PVP at various salt concentrations (at  $-0.75$  v.): 2PVP,  $10^{-3} N$ ;  $\text{Cd}^{2+}$ ,  $10^{-3} M$ ;  $\text{HNO}_3$ ,  $0.1 N$ ; (1)  $\text{KNO}_3$ ,  $0.8 N$ ; (2)  $\text{KNO}_3$ ,  $0.6 N$ ; (3)  $\text{KNO}_3$ ,  $0.4 N$ ; (4)  $\text{KNO}_3$ ,  $0.2 N$ ; (5)  $\text{KNO}_3$ ,  $0.1 N$ ; (6)  $\text{KNO}_3$ ,  $0$ .

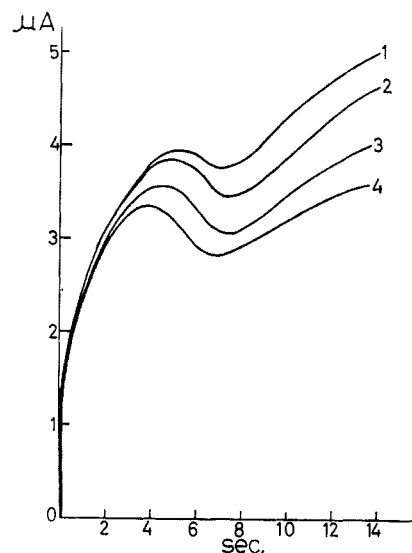


Figure 5. Current-time curves of 4PVP at various salt concentrations (at  $-0.75$  v.): 4PVP,  $7 \times 10^{-4} N$ ;  $\text{HNO}_3$ ,  $0.105 N$ ;  $\text{Cd}^{2+}$ ,  $10^{-3} M$ ; (1)  $\text{KNO}_3$ ,  $0.6 N$ ; (2)  $\text{KNO}_3$ ,  $0.2 N$ ; (3)  $\text{KNO}_3$ ,  $0.1 N$ ; (4)  $\text{KNO}_3$ ,  $0$ .

time curve was greater than in the case of  $\text{Cu}^{2+}$  ( $-0.6$  to  $-1$  v.). Also in this case, at lower acid concentrations, there is a potential dependence of the current across the covered surface. No polarographic

(11) I. R. Miller and A. Katchalsky, *Proc. Intern. Congr. Surface Activity*, 4th, Bruxelles, 1964, in press.

wave could be observed in a 0.15% BSA solution. BSA did not influence the polarographic wave of  $\text{Pb}(\text{NO}_3)_2$ .

### Discussion

It is known from independent measurements (unpublished results) that about 10–14% of the surface area "fully saturated" by 4PVP and a slightly lower fraction of the area covered by 2PVP consists of loopholes, which are accessible to low molecular inert substances or reacting depolarizers. As these loopholes are randomly distributed on the surface, any depolarizer in the near vicinity of the surface may encounter a reaction site. The low concentration of positively charged depolarizers in the layer of positively charged polymeric chains protruding from the surface seems, therefore, to be responsible for the impedance of the surface reaction. This subsurface layer may be of the order of thickness of 50 Å. The diffusion current is assumed to be controlled by the concentration gradient of the depolarizer in this layer, which is low at the moment when surface saturation is just reached, as the outer boundary of the layer is in Donnan equilibrium with a very low local concentration of depolarizer. However, in a very short time, depending on the thickness of the subsurface layer and on the Donnan distribution of the depolarizer on the two sides of the layer boundary, the gradient rises again.

An approximate quantitative treatment of the  $i$ - $t$  curve as a function of the surface concentration of the polyelectrolytes was published in part I of this series. It involves the solution of the Fick differential equation, taking into account the variation with time of the diffusion and distribution coefficients of the depolarizer in the polyelectrolyte surface layer.

For a saturated polyelectrolyte surface layer, a solution of the differential equation can be readily obtained, and the current is given by the approximate expression

$$i_t = 7.08 \times 10^4 n m^{1/2} t^{1/2} D_I^{1/2} C^0 / [1 + (\xi/\kappa D_{II}) \sqrt{D_I/\pi t}] \quad (1)$$

In this equation  $n$  is the number of charges taking part in the electrode process;  $m$  is the rate of flow of mercury in g. sec.<sup>-1</sup>;  $C^0$  is the concentration of the depolarizer in the bulk of the solution;  $D_I$  and  $D_{II}$  are the diffusion constants of the depolarizer in the aqueous solution and in the polymeric surface phase, respectively;  $\kappa$  is the distribution coefficient of the depolarizer between the two respective phases, and  $\xi$  is the thickness of the surface phase. Here  $\kappa = \kappa_{\text{sat}}$  and  $D_{II}$

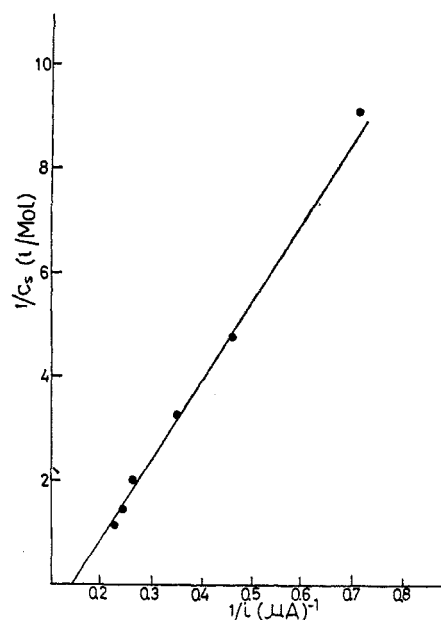


Figure 6 Plot of the reciprocal of the salt concentrations (acid + salt) against the reciprocal of the current (drop age 12 sec.) (values taken from Figure 4): 2PVP,  $10^{-3}$  N;  $\text{Cd}^{2+}$ ,  $10^{-4}$  N.

=  $D_{\text{sat}}$  of part I of this series. Equation 1 is correct only when  $\xi \ll \sqrt{D_I t}$ .

The product  $(\xi/\kappa D_{II})$  can be determined from an analysis of the  $i$ - $t$  curves in the region where the surface reached saturation with regard to the polymer molecules. The time when this saturation point is reached depends again, as pointed out previously,<sup>11</sup> on the polymer concentration and on the diffusion coefficient of the polyelectrolyte.

The distribution coefficient  $\kappa$  can be obtained from the Donnan equilibrium. For the ordinary case when the supporting electrolyte  $C_s \gg C^0$  and when the polyelectrolyte charge concentration in the surface  $\nu \Gamma_p/\xi$  is very high, it is given by

$$\kappa = (C_s/\phi)^z [(\xi/\nu \Gamma_p) - \nu]^z [1 - (\nu \Gamma_p \nu/\xi)] \quad (2)$$

where  $\Gamma_p$  is the polymer surface excess;  $\nu$  is the charge per polymer molecule;  $\phi$  is the osmotic factor of its counterions;  $\nu$  is the volume per residue of a polymeric molecule bearing one charge, and  $z$  is the valency of the depolarizers.

Equations 1 and 2 can be condensed into the form

$$1/i = 1/i_0 + (A/i_0)(1/C_s)^z \quad (3)$$

where

$$i_0 = 7.08 \times 10^4 n m^{1/2} t^{1/2} D_I^{1/2} C^0$$

and

$$A = \xi \phi^2 (D_I / \pi t)^{1/2} / [(\xi / \nu \Gamma_p) - \nu]^2 [1 - (\nu \Gamma_p \nu / \xi)] D_{II}$$

$\log (1/i)$  can be plotted against  $\log (1/C_s)$  whence  $z$  can be evaluated. In the case of  $\text{Cd}(\text{NO}_3)_2$  the valency of the diffusing ionic form of the depolarizer was found to be 1. In Figure 6,  $1/i$  is plotted against  $1/C_s$  for the case of depolarization of  $\text{Cd}^{2+}$  in the presence of 2PVP with nitrate as supporting electrolyte. The

results indicate that  $\text{Cd}^{2+}$  has a tendency to complex formation even with nitrate and that cadmium here is chiefly in the form  $\text{Cd}(\text{NO}_3)^+$ .

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