PULSE POLAROGRAPHY OF HEAVY METAL IONS IN POLYELECTROLYTE SOLUTIONS: BEHAVIOR OF Pb^{2+} AND Cd^{2+} IN PMA SOLUTIONS*

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An orientational study is presented of the pulse polarographic features of Pb^{2+} and Cd^{2+} in aqueous solutions of polymethacrylic acid, partially esterified. Normal pulse polarography with varying pulse duration was applied, and the resulting Cottrell plots were used to check the diffusion-controlled character of the currents. Values for binding constants under various conditions are presented. It could be established that the binding of Pb^{2+} increases with decreasing Pb^{2+}/PMA ratio, which is a typical polyelectrolytic effect. It is in accordance with indications from Henderson–Hasselbalch analysis of the NPP current data. Variation of the pH, corresponding with variation of the overall charge on the polymer, confirms the polyelectrolytic character of the binding. The latter finding is also supported by indications from experiments at different electrolyte concentrations. At rather negative initial potentials and sufficiently low Cd^{2+}/PMA ratio the polarograms for Cd^{2+} show the maxima which are typical for induced reactant adsorption.

In many branches of natural science we have to do with interactions between metal ions and polyelectrolytic substances. Well-known examples are metal complexes of humics in soil waters and surface waters, metalloproteins in biological systems, and metal complexes of synthetic polymers in waste waters[1,2]. Important properties of the heavy metal species, such as mobility, chemical lability and surface activity, are influenced drastically by the (partial) binding to polyelectrolytes. Therefore, the direct electrochemical study of the natural systems has received a growing attention in recent years[3]. A serious complication is the fact that in many cases the polyelectrolytic agents involved are ill-defined in terms of number and nature of active groups which are potentially capable of binding metal ion. Remarkably enough, supporting electrochemical studies of the behaviour of metal ions in solutions of well-defined model polyelectrolytes are very scarce. Yet the need for systematic investigations of the electrochemistry of well-defined metal/polyelectrolyte systems seems to be quite substantial. The aim of the present work is to make an orientational step in this new field.

In this study, the selected model polyelectrolyte is partially esterified polymethacrylic acid. This polymer has been studied in this laboratory[4-6] by using both potentiometric titration methods and rheological techniques. Since the degree of esteri-

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fication is only 33% and the esterified groups are not important for interaction with metal ions, we shall abbreviate here the name of the polymer to PMA (and not to PMA-pe which is frequently found in literature). The groups which are active in metal binding are the aliphatic carboxyl groups; the binding constant for such a ligand may not be expected to be very hith, especially so since the coordination number will be low. The strength of the binding to PMA is comparable with the complexing potentialities of many natural complexing agents. The separation between adjacent carboxyl groups is of the order of 0·5 nm. This could imply that mutual influence of the groups, which essentially gives the polyion its specific features, is effective up to rather high electrolyte concentrations: in a 1 M 1-1 electrolyte solution the Debye screening length is about 0·3 nm, and this is still of the same order as the mean separation of active groups on the polyion. Hence the range of inert electrolyte concentration from 1 molar downwards may be expected to be sensitive to typical polyelectrolytic phenomena.

The binding of heavy metal ions Me^{2+} by polyions of PMA can be written in terms of chemical interaction with the separate carboxyl groups, indicated as COO^-_{PMA}:

$$Me^{2+} + r\,COO^-_{PMA} \rightleftharpoons Me(COO_{PMA})_r^{2-r} . \qquad (1)$$

The conditional stability constant for the complex is denoted as $K'_{1:r}$ and it is defined as the equilibrium constant for the reaction scheme in Eq. (*1*). Obviously, the carboxylic groups on the PMA polyion are also involved in a protolytic equilibrium. Therefore, it is required to carry out experiments at a well-controlled pH. The choice of the optimum pH value for a given metal/PMA system is based on the selection of conditions where metal hydrolysis is at minimum, whereas the dissociation of the PMA carboxyl groups is yet as high as possible. Some indication of the value of such a conditional stability constant might be derived from studies on comparable systems, *e.g.* on Cu^{2+}/polymethacrylic acid, which was investigated by means of viscosimetric, electrophoretic, spectrophotometric and protolytic titration methods[7]. However, in most cases the comparison with earlier studies is only possible for small metal/polyelectrolyte ratios and high absolute values for the polyelectrolyte concentration. Looking at natural systems it seems to be necessary to cover a range of metal/polyelectrolyte ratios as wide as possible and to consider strongly diluted aqueous systems.

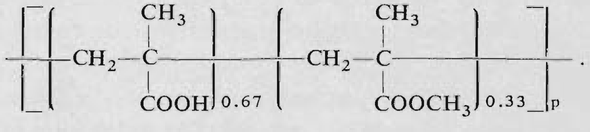
Modern polarographic techniques, rather than potentiometric methods, seem to be suited for the study of heavy metal/polyelectrolyte interactions in a wide range of concentration ratios down to quite low metal ion concentrations. More specifically, it was shown[8,9] that normal pulse polarography (NPP) would be attractive, since it is relatively sensitive and at the same time it offers possibilities to deal with several types of complicating factors in an adequate way. The use of varying pulse duration in NPP provides a means to check whether limiting currents are really diffusion-controlled. If they are not, *e.g.* because of effects due to metal adsorption induced by the surface active polyions, it is often possible to properly correct for this complication and to extract the right answers from the data after all. Furthermore, there is the possibility of selecting different initial potentials in such a way that adsorption effects do not interfere with the limiting currents measured; an extreme case is to choose the initial potential in the limiting current region and to scan in anodic direction (reversed pulse polarography). Another point which must be stressed here is that in cases where (induced) reactant adsorption is likely to occur, NPP compares favorably with the more sensitive differential pulse polarography (DPP). This is so since the former method produces clear warning signs of what is happening (and it is provided with means to deal with it), whereas peak heights rather than peak shapes are generally affected by adsorption in DPP[10], easily leading to incorrect interpretations.

The present study is meant to be a first exploration on the usefulness of pulse polarography for studying metal/polyelectrolyte interactions in aqueous solution. Attention will be given to both the electrochemical aspects and the physico-chemical characteristics of the system. The metal ions Cd^{2+} and Pb^{2+} were chosen in this orientational study, since (*i*) they are amongst the main pollutants of natural waters, (*ii*) they are known to be bound relatively strongly by complexing agents, and (*iii*) they have reasonably well-defined electrochemical properties.

EXPERIMENTAL

Materials

The selected polyelectrolyte, Rohagit S-hv (Röhm GmbH, Darmstadt, FRG), is a copolymer of methacrylic acid and the methyl ester of methacrylic acid. The number ratio of the respective monomeric substances is always about 2. The structural formula may be represented by:



$$\left[\left(-CH_2-\underset{COOH}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-\right)_{0.67}\left(-CH_2-\underset{COOCH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-\right)_{0.33}\right]_p .$$

Detailed descriptions of this copolymer and of its properties have been given in literature[4,5,11]. The average degree of polymerization p is about 10^4, corresponding with a molecular weight of about^6. A solution of the copolymer is prepared by the following procedure. To a weighed amount of the copolymer a strongly alkaline solution is very slowly added under constant stirring, in the dark. This dissolution procedure may be accelerated by heating to about 70°C. It is possible to decrease the degree of neutralization by adding a nitric acid solution, without precipitation down to pH values at least as low as 4. The dilutions of the stock solution of the copolymer used in the experiments showed a viscosity equal to that of pure water. The concentration of the polymer solution is expressed as the molarity at the unesterified carboxylic groups ($COOH_{PMA}$). The concentration of the stock solution was $2 \cdot 0 \, . \, 10^{-2}$M-$COOH_{PMA}$.

The stock solutions of $1 \cdot 0 \, . \, 10^{-2}$M lead(II) nitrate and $1 \cdot 0 \, . \, 10^{-2}$M cadmium(II) nitrate adjusted to different concentrations of potassium nitrate, were prepared from analytical grade chemicals and distilled water.

Nitrogen gas used to remove dissolved oxygen from the sample solutions was purified by passing through a BTS catalyst packed column.

Apparatus

A modified PAR-174A polarographic analyzer was used in the normal pulse mode. The modification enables variation in pulse width and in sampling time[12]. The duration of the time interval between the start of the oulse and the moment at which the current is at its mean value within the sampling period will be defined as the effective pulse duration t_p. Values for t_p are calculated from pulse width and sample duration, assuming a $t^{-1/2}$ dependence of the currrent. The t_p values applied ranged from 14·5 ms to 168·0 ms.

The dropping mercury electrode used was equipped with an automatic drop knocker controlled by the polarograph. A drop time of 2 s was always applied. The surface area of the discarded drops was $1 \cdot 437 \, . \, 10^{-2}$ cm^2.

Measuring procedure

Traces of oxygen were removed from the polarographic cell by passing purified nitrogen gas through the sample solution. During the recording of the polarograms the sample solution was blanketed by a nitrogen gas stream. The polarographic vessel was thermostatted at 25°C. The normal pulse polarograms were recorded on a HP 7040A XY recorded. A saturated calomel electrode was used as a reference; it could be placed directly in the cell since the release of chloride appeared to be negligible for our purposes. All potentials are given with respect to S.C.E. Unless stated otherwise, the initial potential was held at 0·00 V *vs* S.C.E. The scan rate applied was always 5 mV s^{-1}.

RESULTS AND DISCUSSION

A typical picture of the pulse polarographic characteristics of the Pb^{2+}/PMA system is provided by the NP polarograms given in Fig. 1. The shapes of the polarograms are quite regular; only the values of the limiting currents are considerably lower than for the PMA-free lead(II) solution. This is illustrated by looking at the Cottrell plots which are plots of limiting current i_1 against the corresponding values of the reciprocal square root of effective pulse duration $t_p^{-1/2}$. For a diffusion-controlled limiting current the wellknown Cottrell equation holds:

$$i_1 = \pi^{-1/2} n \, F A D^{1/2} C^* t_p^{-1/2} \, , \qquad (2)$$

where A is the electrode surface area, D the diffusion coefficient and C^* the bulk concentration of the electroactive species. Fig. 2 shows that the addition of PMA to a Pb^{2+} solution gives rise to a lowering of the limiting currents while retaining their diffusion-controlled character. It is to be noted that the small intercepts in the Cottrell plots are due to effects of spherical diffusion and drop expansion. It is possible to apply corrections for these effects which results in the disappearance of the intercept. However, for our present purpose it is sufficient to consider the uncorrected Cottrell plot, since we only use the slope which has been shown to be practically unaffected by the corrections[8].

The currents all being diffusion-controlled, it is justified to directly relate the decrease of the slope in the Cottrell plot to the occurrence of binding of Pb^{2+} by PMA. According to Eq. (*1*) we have to do with two types of lead(II) species, *i.e.* Pb^{2+} and $Pb(COO_{PMA})^{2-r}$. Should the $Pb(COO_{PMA})^{2-r}$ complex be labile, then it would contribute to the limiting current and the magnitude of this contribution would be connected with the diffusion coefficient of the complex species. Unfortunately, it is not a simple matter to estimate $D_{Pb(COO_{PMA})^{2-r}}$ *e.g.* from measurements at high concentrations of PMA. On the one hand, the binding of Pb^{2+} to PMA is relatively weak and this means that substantial amounts of free Pb^{2+} are present even at low $[Pb^{2+}]/[PMA]$ ratios (see below for more details on this). On the other hand, the PMA concentration is not allowed to be so very high because this would affect the viscosity of the medium and hence all the diffusion coefficients are altered. Considering the molecular weight

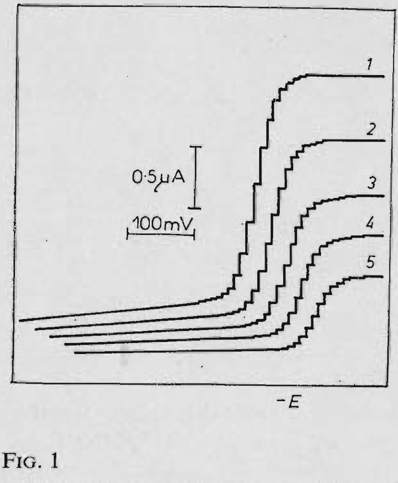


FIG. 1

Normal pulse polarograms for $1{\cdot}0 \cdot 10^{-4}$M Pb^{2+} in the presence of $3{\cdot}0 \cdot 10^{-4}$M $COOH_{PMA}$ and $1{\cdot}0 \cdot 10^{-1}$M-KNO_3. pH 6·0; 25°C; t_p: *1* 14·5 ms; *2* 24·9 ms; *3* 48 ms; *4* 83 ms; *5* 168 ms

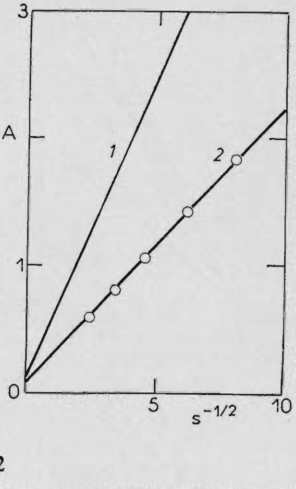


FIG. 2

Comparison of the Cottrell plots for $1{\cdot}0 \cdot 10^{-4}$M-Pb^{2+} in the absence of PMA and in the presence of $3{\cdot}0 \cdot 10^{-4}$M-$COOH_{PMA}$. $1{\cdot}0 \cdot 10^{-1}$M-KNO_3; pH 6·0; 25°C. *1* No PMA; 2 with PMa and the charge, the effective radius of the PMA macromolecule will be such that the diffusion coefficient of the PbPMA species is probably at least two orders of magnitude lower than $D_{\mathrm{Pb}^{+2}}$. Therefore, it seems to be allowed to write

$$D_{\mathrm{Pb(COO_{PMA})_r}^{2-r}} \ll D_{\mathrm{Pb}^{2+}}$$

and to neglect contributions from $\mathrm{Pb(COO_{PMA})_r^{2-r}}$ to the limiting current, certainly as long as the value of i_1 is not very small compared with i_1 for the PMA-free solution.

In parallel with the above there is a problem is establishing the coordination number r in the $\mathrm{Me(COO_{PMA})_r^{2-r}}$ complex. As compared with classical procedures for the determination of r values, studies involving polyelectrolytes are complicated by the finding that the strength of the binding is a function of the metal/polyelectrolyte ratio. An example of such a dependence will be shown below for Pb^{2+}/PMA. We shall see that the assumption of a 1 : 1 binding is in agreement with the experimental data for Pb^{2+}/PMA and Cd^{2+}/PMA. However, at this moment the possibility of $r = 2$, for which some indication has been given with respect to the Cu^{2+}/PMA complex

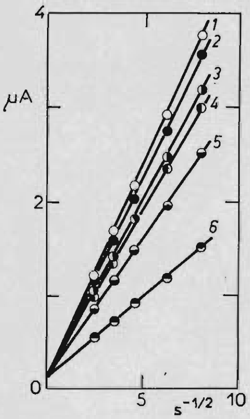


FIG. 3

Cottrell plots for 1·0 . 10^{-4} Cd^{2+} in the presence of different concentrations of $\mathrm{COOH_{PMA}}$. 1·0 . 10^{-1}M-$\mathrm{KNO_3}$; pH 8·5; 25°C. Concentration of $\mathrm{(COOH)_{PMA}}$ (mol/dm³): *1* 0; *2* 2 . 10^{-5}; *3* 6 . 10^{-5}; *4* 1 . 10^{-4}; *5* 2 . 10^{-4}; *6* 5 . 10^{-4}

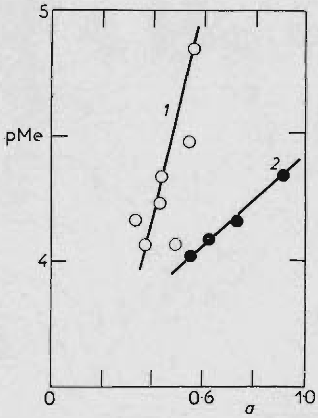


FIG. 4

Henderson–Hasselbalch plots for Pb^{2+} : : $\mathrm{COOH_{PMA}}$ and $\mathrm{Cd}^{2+}/\mathrm{COOH_{PMA}}$. *1* 1·0 . 10^{-4}M-Pb^{2+}; 1·0 . 10^{-2}M-$\mathrm{KNO_3}$; $\mathrm{COOH_{PMA}}$ concentrations varying from 5·0 . 10^{-5} to 4·0 . 10^{-4}M; pH 6·0; 25°C. *2* 1·0 . 10^{-4}M-Cd^{2+}; 1·0 . 10^{-1}M-$\mathrm{KNO_3}$; $\mathrm{COOH_{PMA}}$ concentrations varying from 2·0 . . 10^{-5} to 5·0 . 10^{-4}M; pH 8·5; 25°C at higher PMA concentration[7], cannot be ruled out. Part of our future studies will be aimed at finding subtle solutions to this problem. In the following we shall consider the interaction to take place between one Pb^{2+} ion and one carboxyl group. The corresponding stability constants will be denoted as $K'_{1:1}$.

Applying Eq. (*1*) to the data in Figs 1 ynd 2 leads to a value for $K'_{1:1}$ of $0{\cdot}5 \,.\, 10^4$. This value holds for the specific conditions that $Pb^{2+}_{tot}/PMA_{tot} = 0{\cdot}33$, pH = 6·0 and $[KNO_3] = 0{\cdot}1$ M. Apparently, the binding of Pb^{2+} to PMA is rather weak, reflecting the observation that *e.g.* about 50% of the Pb^{2+} remains free in solution when a threefold excess of PMA is present. The magnitude of this $K'_{1:1}$ for Pb^{2+}/PMA seems to be reasonable as compared with the somewhat lower value for the corresponding monomeric aliphatic acid ($\log K'_{1:1}$ of the order of 2·5 (ref.[13]).

Metal/polyelectrolyte ratio

In Fig. 3, the Cottrell plots are shown for $1{\cdot}0 \,.\, 10^{-4}$ M-Cd^{2+} at different PMA concentrations, ranging from $2{\cdot}0 \,.\, 10^{-5}$ to $5{\cdot}0 \,.\, 10^{-4}$ M-$COOH_{PMA}$. The data indicate that the limiting currents are diffusion-controlled. From the plots it appears that the calculated values for $K'_{1:1}$ are about $0{\cdot}3 \,.\, 10^{+4}$, quite independent of the Cd^{2+}/PMA ratio. In the case of Pb^{2+}/PMA, at pH = 6·0 and $1{\cdot}0 \,.\, 10^{-2}$ M KNO_3, the $K'_{1:1}$ value increased from $0{\cdot}5 \,.\, 10^{+4}$ to $2{\cdot}4 \,.\, 10^{+4}$ in the concentration ratio range 2 : 1 to 1 : 4, at constant total concentration of $1{\cdot}0 \,.\, 10^{-4}$ M lead(II).

The stability constant is sensitive to the Me/PMA ratio in the system Pb^{2+}/PMA, whereas in the system Cd^{2+}/PMA it is not. The metal/polyelectrolyte ratio is linked with the degree of "occupation" at the polyion by metal ions. Generally, in a system showing polyelectrolyte features, the stability constant will decrease as more metal ions are bound to the polyion. This is due to the decrease in the overall negative charge on the polyion, caused by the metal binding.

For polyelectrolytic systems, the equilibrium constant according to Eq. (*1*) is empirically rewritten as[14]

$$\mathrm{pMe} = \log K'_{1:1}\,(\mathrm{intr.}) - n \log\left([\mathrm{MeCOO}^{+}_{\mathrm{PMA}}]/[\mathrm{COO}^{-}_{\mathrm{PMA}}]\right). \qquad (3)$$

The parameter *n* is a constant depending on the extent of interaction between the different binding sites on the polyion. For simple electrolytes *n* is unity.

The difference between the Pb^{2+}/PMA and Cd^{2+}/PMA interactions is visualized in Fig. 4, where Henderson–Hasselbalch plots according to Eq. (*3*) are shown. From the plots it is tentatively concluded that, under the experimental conditions, the PMA polyions show a more pronounced polyelectrolytic type of interaction with Pb^{2+} ions, compared with Cd^{2+} ions. This finding will be given attention in future studies.

Base Electrolyte Concentration

Cottrell plots for Pb^{2+}/PMA at a fixed concentration ratio are shown in Fig. 5 at different concentrations of KNO_3. The limiting currents are diffusion-controlled. Below 10^{-2} M-KNO_3 (with $[Pb^{2+}] = 1{\cdot}0 \,.\, 10^{-4}$ M) migrational mass transport of the electroactive species becomes important. This gives rise to increased limiting currents which do not obey Eq. (*2*). Fortunately, it is still possible to utilize data for very low inert electrolyte concentrations[15] and we will devote a separate study to this aspect. From the Cottrell plot, the corresponding $K'_{1:1}$ values are calculated and plotted in Fig. 6, graph *a*. It is clear that $K'_{1:1}$ decreases with increasing salt concentration. Whether this decrease in $K'_{1:1}$ is due to polyelectrolytic features of the system or to decreasing activity coefficients at higher salt concentration can be explored by using activities instead of concentrations in he calculation of $K'_{1:1}$. Correction for activity effects, however, is not simple in the case of polyelectrulytic components. As a first approximation it was assumed that the activity coefficients $\gamma_{PbCOO_{PMA}^+}$ and $\gamma_{COO_{PMA}^-}$ are equal. Then the corrected stability constant follows from $K'_{1:1,corr} = K'_{1:1}/\gamma_{Pb^{2+}}$. The activity coefficient of Pb^{2+} was calculated according to Debye–Hückel[16] (graph *b*) and Davies[17] (graph *c*), respectively. In both cases, the magnitude of the dependence of $K'_{1:1,corr}$ upon the neutral salt concentration is substantially reduced. The remaining increase of $K'_{1:1,corr.}$ with decreasing electrolyte concentration

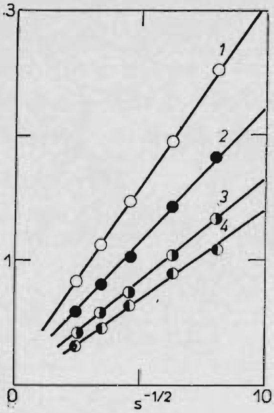


FIG. 5

Cottrell plots for $1{\cdot}0 \,.\, 10^{-4}$M-Pb^{2+} in the presence of $3{\cdot}0 \,.\, 10^{-4}$M-$COOH_{PMA}$ at different concentrations of KNO_3. pH 6·0; 25°C. Concentration of KNO_3 (mol/dm^3): *1* 1·0; *2* 1 . 10^{-1}; *3* 1 . 10^{-2}; *4* 1 . 10^{-3}

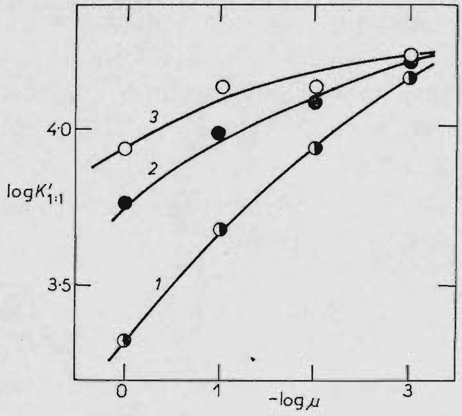


FIG. 6

1 Dependence of the apparent stability constant $K'_{1:1}$ for $PbCOO^+_{PMA}$ upon base electrolyte concentration (μ). *2* Idem, using activities according to Debye–Hückel. *3* Idem, using activities according to Davies could be related with the polyelectrolytic character of the complexing agent. It would be related to the screening of charged groups on the polyion by the inert electrolyte in solution. The effect of screening is reduced, *i.e.* the interaction between the groups is increased, when the electrolyte concentration is lowered.

pH Dependency of $K'_{1:1}$

The polyelectrolytic features of the Pb^{2+}/PMA system are also illustrated by plotting the $K'_{1:1}$ values, evaluated for a fixed Pb^{2+}/PMA ratio and for one electrolyte concentration, against pH. Fig. 7 shows that $K'_{1:1}$ is drastically influenced by the pH of the solution. Partly, this influence is to be explained by the fact that the actual complexing agent, *i.e.* the COO^-_{PMA} group, is not fully dissociated in the pH range considered. However, we can easily eliminate this protolytic effect by considering $K'_{1:1}/\alpha$ instead of $K'_{1:1}$ itself (with α being the degree of dissociation of the $COOH_{PMA}$). Values for α at different pH values can be estimated from the protolytic titration curves given by Böhm[4]. It appears that the pH range covered corresponds with the region around $\alpha = 0{\cdot}5$. Note that the change of α with pH is less strong with polyelectrolytes than it is with simple electrolytes. For the data in Fig. 7 this has the con-

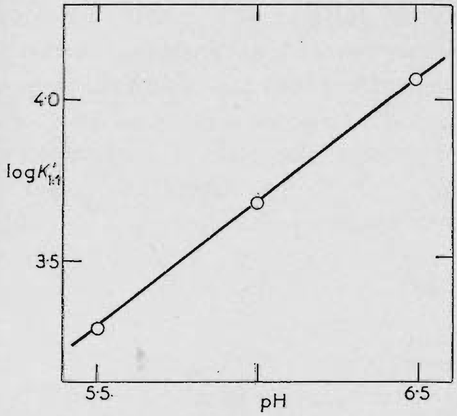


FIG. 7

Dependence of the apparent stability constant $K'_{1:1}$ for $PbCOO^+_{PMA}$ upon the pH. The total concentrations of lead(II) and PMA are $1{\cdot}0 \,.\, 10^{-4}$M and $4{\cdot}0 \,.\, 10^{-4}$M respectively and the KNO_3 concentration is $1{\cdot}0 \,.\, 10^{-1}$M

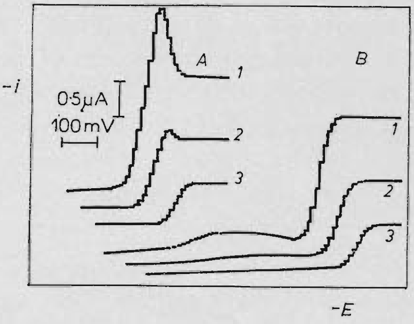


FIG. 8

Normal pulse polarograms for $1{\cdot}0 \,.\, 10^{-4}$M Cd^{2+} in the presence of $5{\cdot}0 \,.\, 10^{-4}$M $COOH_{PMA}$ and $1{\cdot}0 \,.\, 10^{-1}$M-KNO_3 pH = = 8·5; 25°C. *A* E_i = —0·40 V *vs* S.C.E.; *B* E_i = 0·00 V *vs* S.C.E. t_p: *1* 14·5 mst 2 48 ms; *3* 168 ms sequence that the extent of the dependence of $K'_{1:1}$ on pH is decreased by about 50%. The remaining increase of binding strength with increasing pH can be explained in terms of the polyelectrolytic properties of the complexing agent: as the (negative) charge on the polyion increases with increasing pH, the mutual repulsion of the COO^-_{PMA} groups becomes more severe and hence the tendency to bind cations increases, leading to a higher value of $K'_{1:1}$. This feature runs parallel with our findings for a varying Pb^{2+}/PMA ratio (see above).

Induced Metal Ion Adsorption

The system Cd^{2+}/PMA shows some of the features which are characteristic for (induced) reactant adsorption. As is shown in Fig. 7, the shape of the NP polarogram is rather strongly dependent on the initial potential E_i. Comparing the polarograms at a fixed t_p for $E_i = -0.40$ V *vs* S.C.E. and $E_i = 0.00$ V *vs* S.C.E. respectively, we see that it is the more negative E_i which gives rise to typical (induced) reactant adsorption maxima. These maxima are sometimes denoted as Barker–Bolzan peaks[18], after their discoverers[19], and they are caused by the extra amount of metal ions present in the adsorbed state. The correctness of the interpetation of the observed phenomena in terms of adsorption is confirmed by the strong dependence of the height of the maximum on the pulse duration and also by the presence of an adsorption hump in the baseline around -0.40 V in the polarograms for $E_i = 0.00$ V *vs* S.C.E.

It should be stressed that the effects observed reflect the *induced* adsorption of the metal ions and *not* the adsorption of the PMA polyions. For instance, it is quite likely that the negatively charged PMA entities are more strongly adsorbed at 0·00 V (where we have a positively charged electrode surface) than at -0.40 V. However, the positive charge on the electrode at 0·00 V *vs* S.C.E. repels the divalent metal cations so that no surface complexation of metal and polyion takes place. This explains the regular shapes of the polarograms for $E_i = -0.00$ V. Apart from this potential effect, the magnitude of metal ion adsorption increases with increasing PMA concentration and it also increases with decreasing ionic strength. Both observations are in accordance with the idea of induced Cd^{2+} adsorption, since in both cases the number of Cd^{2+} ions in the adsorbed layer is increased.

On the basis of the difference in $K'_{1:1}$ values for Pb^{2+}/PMA and Cd^{2+}/PMA it could be expected that for Pb^{2+} the adsorption effects are even more pronounced. We have not been able to extract evidence for this from the available polarograms. We should keep in mind that the pH of Pb^{2+}/PMA solutions was always some 2·5 units lower than the pH of the Cd^{2+}/PMA solutions. Therefore, the values for lead(II) refer to a situation where the polyions carry less charge which could lead to a weaker adsorption at more positive electrode potentials. The initial potential for all the Pb^{2+}/PMA polarograms was 0·00 V and at this E_i value the Cd^{2+}/PMA system behaves normally as well (Fig. 8). Apparently the Pb^{2+} ion, which does form the stronger bonds with PMA, is not capable of crossing the electrostatic energy barrier imposed by the electrode charge at the initial potential.

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