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Inhibitory Effect of Amines on Polarographic Processes in Acid Solution. II. A. C. Polarographic Investigation

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The inhibiting properties of several amines as surface active substances and as corrosion inhibitors in acid solution was studied by the a. c. polarographic method. The electrode processes of cadmium and lead served as indicators of the inhibitor efficiency. The inhibitions of the electrode processes, resulting in a decrease of the a. c. polarographic wave, was found to increase in the sequence: *n*-butylamine < pyridine < aniline < *o*-methylpyridine < *o*-toluidine < 2,3-dimethylaniline < 2,6-dimethylaniline < < quinoline < α-napthylamine. The investigations were performed in 1 *N* $HClO_4$, H_2SO_4 or H_3PO_4. A stronger inhibitor efficiency was found in the H_3PO_4 solution. The relation between the inhibition and the *p*H of the solution showed that the RNH_3^+ ion inhibited considerably more than the neutral RNH_2 molecules. The influence of chloride ion on the rate of inhibited electrode processes was also investigated. It has been found that the accelerating effect does not depend on the nature of the investigated amines and that there is a linear relation between the accelerating effect and the chloride concentration.

The results of investigations of the inhibitory effect of several amines on polarographic processes in acid solution, studied by the d. c. polarographic and oscillopolarographic method, were given in a former publication[1]. Present paper comprises analogous investigations by the alternating current (a. c.) polarography.

B. Breyer and S. Hacobian[2], S. L. Gupta and S. K. Sharma[3], H. Jehring[4] and others[5] have studied the influence of surface active substances on the a. c. polarographic waves of some metallic cations (such as Ti^+, Cu^{2+}, Cd^{2+}, Zn^{2+}, Mn^{2+}). It has been found that in most cases the surface active substance decreases the a. c. wave, due to the fact that the formed adsorbed film hinders the rate of electron transfer (owing to the presence of a charged barrier at the electrode)[2] so much that it becomes slower than the diffusion rate, *i. e.* the irreversibility of the electrode reaction increases and, consequently, the a. c. wave decreases. The extent of inhibition in the kinetics of the electrode process depends on the concentration of the surface active substance and on the structure of the adsorbed film, *i. e.* on the nature of the surface active substance (especially its charge) and the nature of the reducible species. There has been found[4,6] a correspondence between adsorption isotherms, $\Theta = f\ (C_{inh})$, obtained from the surface coverage Θ, which was calculated from the extent of inhibition ($\Theta = (i^o - i)/i^o$, where i is the current in the presence and i^o in the absence of surface active substances) and which was also calculated from the decrease of the differential capacity ($\Theta = (C_D^o - C_D)/(C_D^o - C_D^S)$, where C_D^o is the differential capacity in the absence of surface active substance and C_D^S corresponds to the complete surface coverage).

This paper presents the results of investigations of the influence of several amines on a. c. polarographic waves of Pb^{2+} and Cd^{2+} ions in 1 N $HClO_4$, H_2SO_4 and H_3PO_4. The influence of acid concentration on the inhibition of a. c. polarographic processes of the quoted ions was also investigated. Parallelly with a. c. polarographic investigations, the measurement of differential capacity of the electric double-layer were performed in order to relate the inhibiting efficiency of amines with their effects on the differential capacity. Finally, the accelerating effect of chloride ions on the inhibited a. c. polarographic process was investigated.

EXPERIMENTAL

The differential capacity of the double-layer and the a. c. polarograms (*i. e.* the capacity component of the electrode reaction) were recorded with the polarograph Polariter PO-4 with a supplementary device after Kowalski and Srzednicki[7] and Valeriot and Barradas[8]. The superimposed alternating voltage was 8 mV and the frequency was 40 Hz. With the same polarograph were recorded d. c. polarograms and potential-sweep chronoamperograms. The employed voltage sweep rate was 0.0133 v./sec. The oscillopolarographic measurements were performed as described earlier[1]. Polarographic current-time curves were obtained by means of an Orion Oscilloscope, Model TR-4401. The current-time curves were recorded with the »first drop«, applying the device described by L. Nemec and L. Smoler[9].

The dropping mercury electrode (DME) of the following characteristics was used: m = 1.79 mg/sec and t = 4.74 sec in 0.1 *M* KCl, measured with open circuit at h = 43 cm. The hanging mercury drop electrode (HMDE) was prepared after Kowalski and Srzednicki[6] with a modification necessary to obtain a higher exactness in reproducing the surface of the mercury drop. The mercury drop surface was 2.36 mm^2.

The polarographic cell and other equipment did not differ from that described in a previous paper[10]. The circuit impedance was made small for a. c. measurements by shunting the mercury pool and the reference cell with a condenser[11]. All potentials are given with respect to the calomel electrode prepared with a saturated solution of sodium chloride. All measurements were carried out under the constant temperature of 25 ± 0.1° C.

For the preparation of solutions analytical grade chemicals ($HClO_4$, H_2SO_4, H_3PO_4, HCl, NaCl, $NaClO_4$) were used. The solutions of cadmium and lead perchlorates were prepared by dissolving corresponding oxides in perchloric acid. The concentration of cadmium and lead for polarographic measurements was 0.4 m*M*. Amines were dissolved in an equivalent amount of acid. The following amines were used: *n*-butylamine (nBA) puriss. grade, triethylamine (TEA) analytical-grade, aniline (An) analytical-grade, *o*-toluidine (oT) puriss. analytical grade, 2,3-dimethylaniline (2,3DMAn or oXy) puriss. grade, 2,6-dimethylaniline (2,6DMAn or mXy) puriss. grade, α-naphthylamine (αNA) analytical-grade, pyridine (Py) analytical-grade, *o*-methylpyridine (oMPy or αP) purum grade and quinoline (Q) purum grade, all of the Fluka firm. Redistilled water and redistilled mercury were used.

RESULTS

Alternating current (a. c.) polarographic measurements were performed with the dropping mercury electrode (DME) and with the hanging mercury drop electrode (HMDE). For comparison, direct current (d. c.) polarographic measurements were also made with DME and HMDE (potential-sweep chronoamperometry), as well as oscillopolarographic measurements (but only with triethylamine, 2,3- and 2,6-dimethylaniline and *o*-methylpyridine). The extent of inhibition is expressed in per cent decrease of the polarographic wave of cadmium and lead ($(i_0 - i)\,100/i_0$, where the zero index refers to the current in the absence of the inhibitor).

Perchloric acid solutions. — Some of results of investigation in 1 *N* $HClO_4$ are given in Figs. 1—4. It is evident that the inhibition curves (isotherms) obtained with HMDE are shifted to lower concentrations of amines with regard to those obtained with DME, this being the case for the d. c. as well as for the a. c. polarographic waves of cadmium and lead. The slopes of the plots are the same in both cases.

The a. c. polarographic wave is extremely sensitive to adsorption of amines on the electrode surface. The inhibition curves of a. c. waves are shifted by an order of magnitude towards lower concentrations of amines with regard to the inhibition curves of d. c. waves of both cadmium and

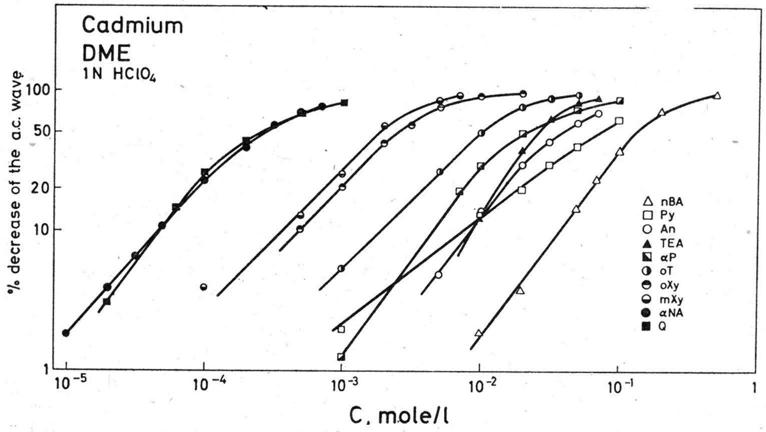


Fig. 1. Decrease of a. c. polarographic wave of cadmium as a function of amine concentration.

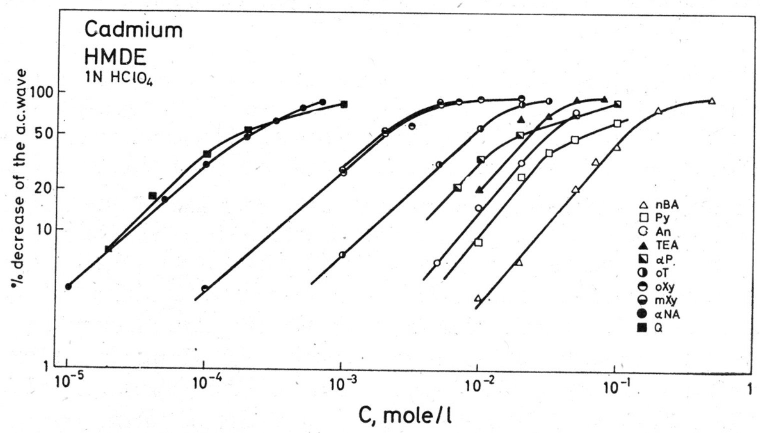


Fig. 2. Decrease of a. c. polarographic wave (with HMDE) of cadmium as a function of amine concentration.

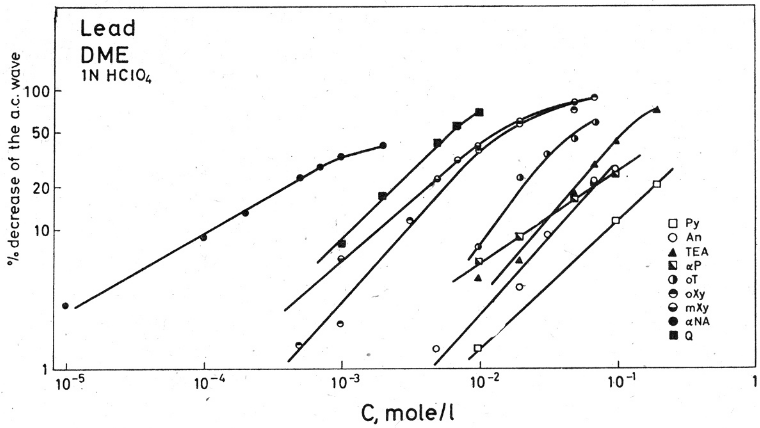


Fig. 3. Decrease of a. c. polarographic wave of lead as a function of amine concentration.

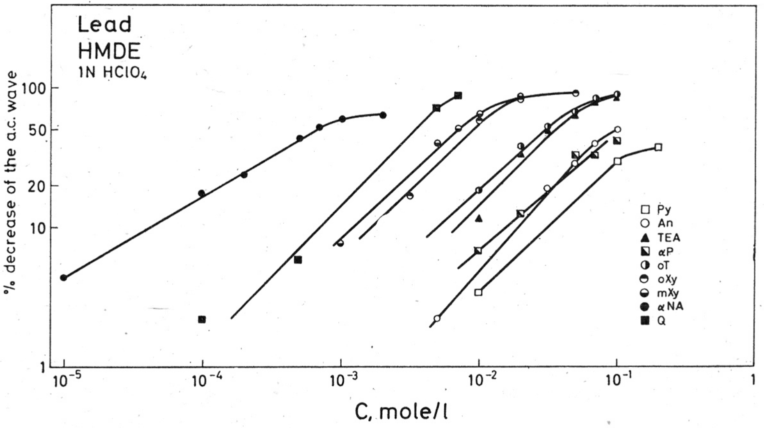


Fig. 4. Decrease of a. c. polarographic wave (with HMDE) of lead as a function of amine concentration.

of lead[1]. However, the cadmium a. c. wave is considerably more sensitive to the inhibitor than the lead a. c. wave, this being the case with their d. c. waves as well[1]. The slopes of inhibition curves for cadmium and lead is for most of the investigated amines the same, with the exception of αNA.

The inhibition efficiency, *i. e.* the per cent decrease of the cadmium a. c. wave as a function of the concentration of amine, increases in the sequence: *n*-butylamine $<$ pyridine $<$ aniline $<$ triethylamine $<$ *o*-methylpyridine $<$ $<$ *o*-toluidine $<$ 2,3-dimethylaniline $<$ 2,6-dimethylaniline $<$ quinoline, α-naphthylamine. The same order is valid for the lead a. c. wave with the difference that α-napthylamine is a considerably stronger inhibitor than quinoline. Oscillopolarographic measurements of the extent of inhibition of triethylamine, 2,3- and 2,6-dimethylaniline are also in accordance with the quoted order as well.

Sulphuric acid and posphoric acid solutions. — Fig. 5 represents a comparison of investigations in 1 *N* $HClO_4$, 1 *N* H_2SO_4 and 1 *N* H_3PO_4 for some of the investigated amines. It can be seen that the extent of inhibition of amines on the cadmium a. c. polarographic process in 1 *N* H_3PO_4 is stronger than in 1 *N* $HClO_4$ and 1 *N* H_2SO_4. The difference between $HClO_4$ and H_2SO_4 is considerably smaller though expressive. Inhibition curves in H_2SO_4 are less steep, so that in lower concentration ranges of amines the extent of inhibition is stronger and in the higher ones weaker than in $HClO_4$. The slope of inhibition curves in 1 *N* H_3PO_4 is for most amines (except for *n*-butylamine) the same as in 1 *N* $HClO_4$.

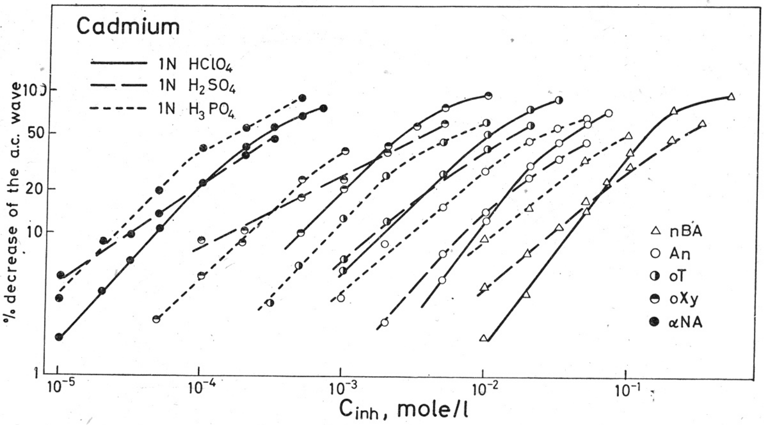


Fig. 5. Comparison of decrease of a. c. polarographic wave of cadmium in 1 N $HClO_4$, H_2SO_4 and H_3PO_4 as a function of amine concentration.

The influence of acid concentration. — The influence of the concentration of acid on the extent of inhibition of a. c. polarographic processes of cadmium and lead has been investigated with two amines, *i. e.* with aniline and α-naphthylamine in perchloric acid solutions. By addition of sodium perchlorate the ionic strength of solutions was kept at constant value 1. The results of investigations are represented in Figs. 6 and 7. It can be seen that the inhibition of a. c. polarographic processes of cadmium and lead depends greatly on the *p*H of the solution, *i. e.* on the concentration of amine (RNH_2) and of aminium ion (RNH_3^+) in solution. Equivalence points are marked with arrows in Figs. 6 and 7.

With α-naphthylamine the maximum inhibitory effect occurs at *p*H 4.5 for cadmium and lead. Consequently, the strongest inhibitory effect is obtained when almost all RNH_2 is converted into RNH_3^+ ion. By the decrease of the concentration of RNH_3^+ ion, resp. by the increase of the concentration of RNH_2, the inhibition of electrode reaction decreases very rapidly. However, in the presence of RNH_3^+ ions the inhibition of electrode process decreases, though more slowly, with the increase of the concentration of acid.

Aniline behaves quite differently. The inhibition of the electrode reaction of cadmium increases with the decrease of concentration of RNH_2, or with

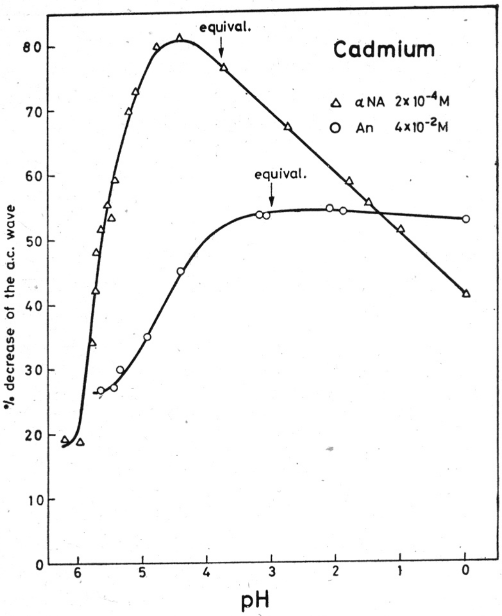


Fig. 6. Decrease of a. c. polarographic wave of cadmium as a function of pH of the amine solution.

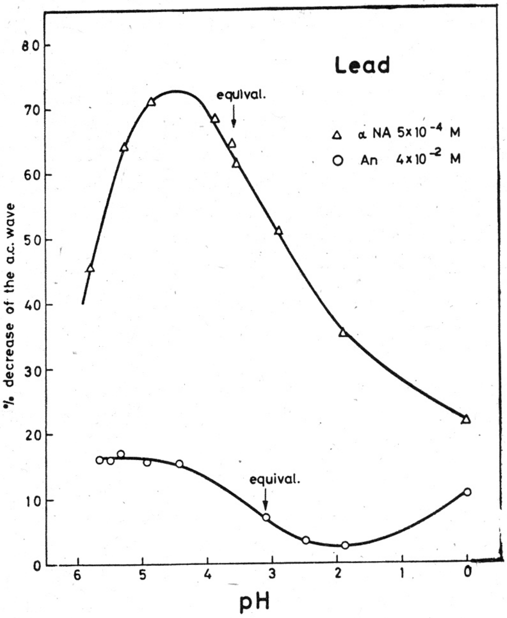


Fig. 7. Decrease of a. c. polarographic wave of lead as a function of pH of the amine solution.

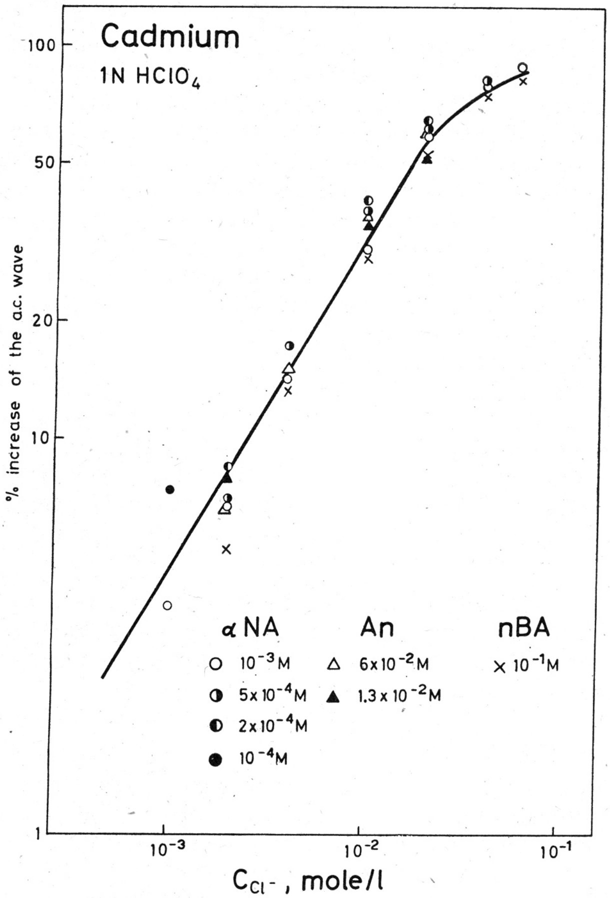


Fig. 8. Increase of inhibited a. c. polarographic wave of cadmium as a function of the chloride ion concentration.

the increase of concentration of RNH_3^+, it is maximal at the equivalence point and does not change with a further increase of the concentration of acid. However, the inhibition of electrode reaction of lead increases with the increase of concentration of RNH_2 ($pH > 3$) and when the concentration of RNH_3^+ is very small the inhibition reaches the maximum value. When only RNH_3^+ ($pH < 3$) is present in the solution the inhibition decreases with the increase of concentration of acid to pH 2 and then increases again.

The influence of chloride ion on inhibited electrode process. — The influence of chloride ion on the a. c. polarographic electrode process of cadmium was investigated in 1 N $HClO_4$ which was inhibited with *n*-butylamine, aniline, or α-naphthylamine. The results of investigations are represented in Fig. 8. It can be seen that the inhibiting effect of amines decreases with the increase of the concentration of chloride, *i. e.* the rate of inhibited electrode process increases with the increase of the concentration of chloride.

DISCUSSION

From the obtained results of measurements it can be concluded that the a. c. polarographic method is a considerably more sensitive method for evaluating the inhibitory properties of amines in acid solutions than the d. c. polarographic and oscillographic methods. The higher sensitivity of the method with HMDE is compensated by the simplicity of the work with DME. Since the inhibition curves are of the same slopes and courses, the higher sensitivity of HMDE is certainly due to the greater possibility of establishing adsorption equilibrium. Further investigations are in progress. Recorded polarographic current-time curves have shown that the surface coverage is limited by adsorption equilibrium[12]. With the increasing concentration of a strongly surface active amine (for instance, α-naphthylamine) the current of cadmium not only decreases but becomes progressively more independent of the height of the mercury reservoir. Thus with the concentration of α-naphthylamine of 1.7×10^{-2} M the current of cadmium is completely independent of the height of the mercury reservoir and the parabolic i—t curve (for limiting current) corresponds to the equation $i = k \times t^{0.61}$, therefore behaving as a kind of kinetic current. With concentrations of α-naphthylamine higher than 10^{-2} *M* the shape of i—t curves indicates that the surface coverage is limited by adsorption rate and adsorption equilibrium[12].

The extent of inhibition of the cadmium and lead a. c. waves runs parallel to the surface coverage[13] (Fig. 9). Surface coverage has been determined at the potential of the point of zero charge. This can also be seen from the change of differential capacity with the change of the concentration of amines (Figs. 10 and 11) in the range of the potential of electrode reactions of cadmium and lead.

The inhibition of the a. c. polarographic wave of lead with all investigated amines is less intensive than for cadmium, as has been found in d. c. polarographic and oscillopolarographic investigations[1] as well. It is due to the smaller surface coverage (apparent surface coverage[14]) of the electrode at more positive potentials than the point of zero charge (Fig. 12). However, for aniline, o-toluidine, and α-naphthylamine, which, due to π-electronic interactions with the surface of mercury at potentials on the positive side

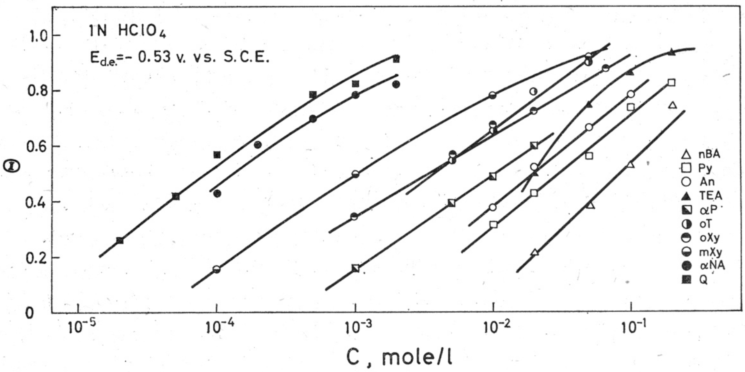
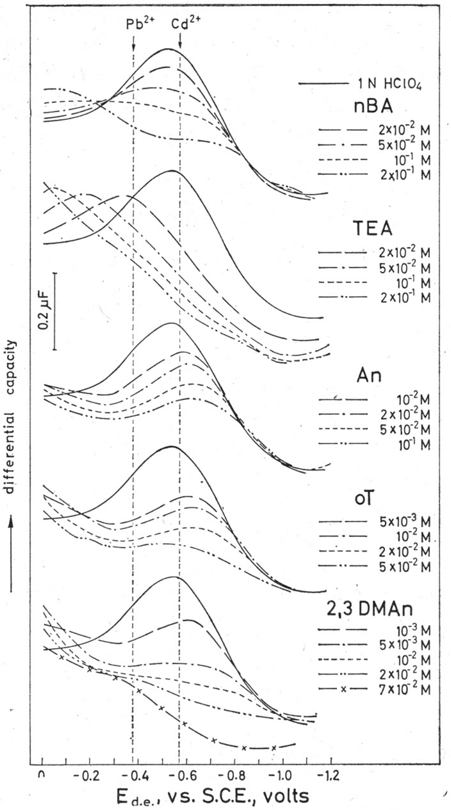


Fig. 9. Surface coverage as a function of the amine concentration.



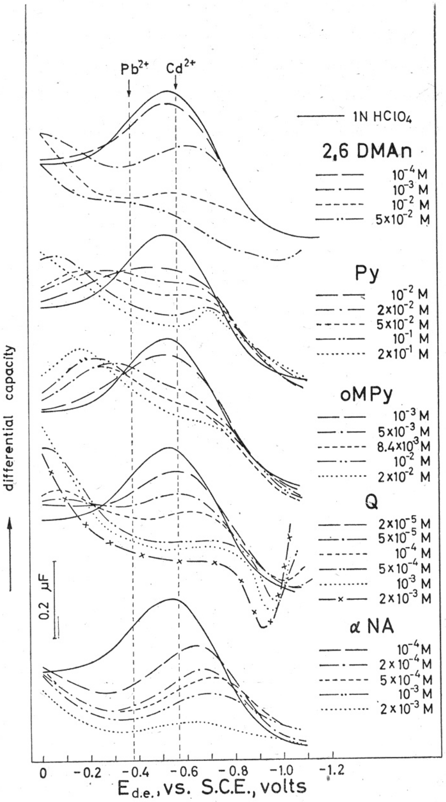


Fig. 10. Differential capacity curves of 1 N $HClO_4$ and of 1 N $HClO_4$ with additions of amines (DME).

Fig. 11. Differential capacity curves of 1 N $HClO_4$ and of 1 N $HClO_4$ with additions of amines (DME).

of the electrocapillary curve, give an even higher surface coverage at the potential of electrode reaction of lead than that of cadmium, another factor, besides surface coverage, should be considered. This is probably a generally greater electrode reaction rate of the reduction of lead[15] and the extent of inhibition of the lead a. c. wave is, generally, smaller than that of the cadmium a. c. wave. The difference between the actions of quinoline and α-naphthylamine on the a. c. waves of cadmium and lead (Figs. 1—4) is due, as can be seen from Fig. 12, to the extent of surface coverage in these two cases.

The inhibition of the cadmium electrode reaction in perchloric and sulphuric acid solutions differ only slightly, still the inhibition in sulphuric acid is somewhat stronger. However, the inhibition in phosphoric acid is substantially stronger than in the two mentioned acids. This phenomenon is well-known in corrosion literature[16] for other kinds of corrosion inhibitors as well. It is certainly due to the change of hydrogen ion concentration (Fig. 6). Thus the inhibition efficiency of 4×10^{-2} *M* aniline and 2×10^{-4} *M* α-naphthylamine in 1 *N* H_3PO_4 for cadmium is 62%, and 56% respectively, whereas in $NaClO_4 + HClO_4$ solution of the same *p*H (1.25) it is 54%, and 53% respectively. Accordingly, the change of the hydrogen ion concentration seems to be the main but not the only cause of this phenomenon. Further investigations are in progress.

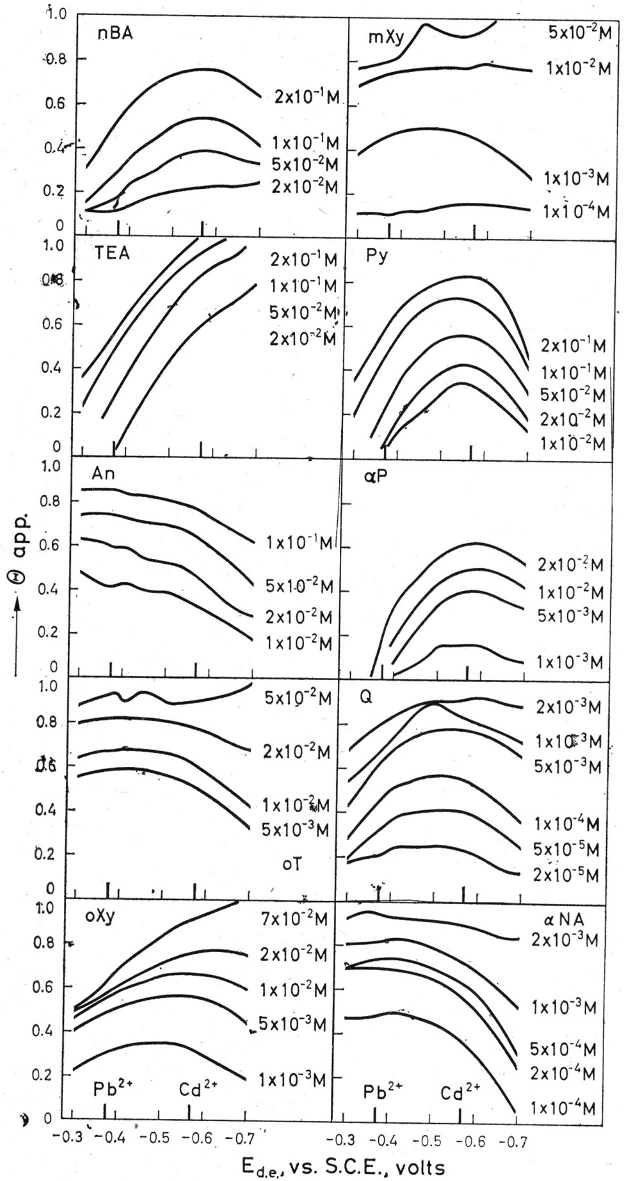


Fig. 12. Apparent surface coverage as a function of potential.

The influence of the concentration of acid or — more exactly — the *p*H of the solution, on the inhibition efficiency of amines (Figs. 6 and 7) is of special interest. According to Blomgren and Bockris[13] the amines are preferentially electrosorbed as RNH_3^+ ions from 0.1 *N* HCl solution. However, investigations of Djatkina and Damaskin[17] have shown that differential capacity decreases in HCl + KCl solutions of aniline mainly by adsorption of neutral molecules $C_6H_5NH_2$. Our investigations of the change of differential capacity with the change of the *p*H of the solutions of aniline and α-naphthylamine (Figs. 13 and 14) are in accordance with the results of the Russian authors. With the increase of *p*H, i. e. with the increase of the concentration of organic bases (RNH_2), or with the decrease of the concentration of their conjugate acids (RNH_3^+), the differential capacity is lowered considerably. Corresponding to the adsorption of neutral molecules RNH_2, the decrease of C_D is the highest at the potential of e. c. m. However, from C_D—E curves is also visible a strong adsorption of RNH_3^+ ions, which are formed in acid solutions exclusively. At the potential of discharge of lead practically no change of C_D occurs with the change of *p*H of the solution containing aniline (Fig. 13). This means that, at that potential, there is a negligible difference in adsorption of $C_6H_5NH_2$ molecules and $C_6H_5NH_3^+$ ions. A slight change of the extent of inhibition of the lead a. c. wave with the change of *p*H of the solution of aniline (Fig. 7) is also in accordance with this fact. However, though the change is slight, still the extent of inhibition is markedly greater in the *p*H range in which only

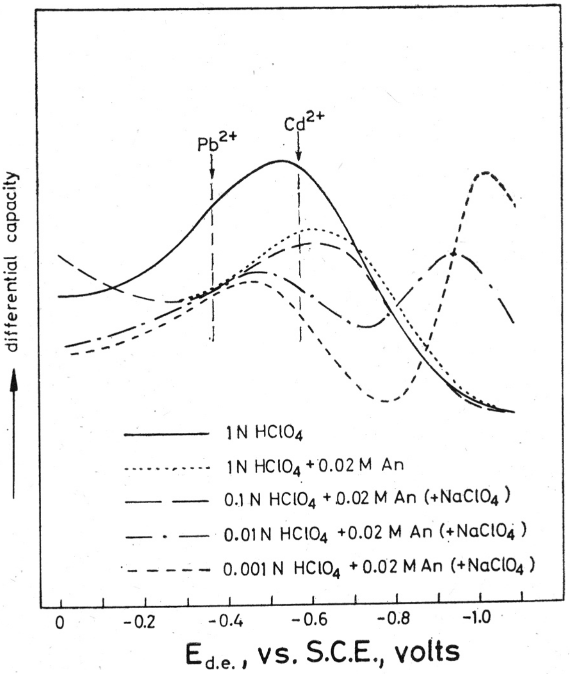


Fig. 13. Differential capacity curves of 1 N $HClO_4$ and of 0.001—1 N $HClO_4$ with addition of aniline (DME).

neutral $C_6H_5NH_2$ molecules can be adsorbed. Quite different is the inhibition of the cadmium a. c. wave (Fig. 6). The extent of inhibition increases with the increase of the concentration of $C_6H_5NH_3^+$ ions, or with the decrease of the concentration of the neutral $C_6H_5NH_2$ molecules. Fig. 15 represents experimental and calculated inhibition curves for that case. The calculated curve was obtained by applying the dissociation constant of aniline and under the assumption that in 1*N* $NaClO_4$ practically all of the aniline is present in the form of $C_6H_5NH_2$ molecules, and in 1*N* $HClO_4$ in the from of $C_6H_5NH_3^+$ ions. It can be seen that the curves are in good correspondance. Accordingly, the electrode reaction of cadmium is inhibited considerably more by $C_6H_5NH_3^+$ ions than by $C_6H_5NH_2$ molecules. This is probably in connection with the difference in double-layer structure, because if the inhibitor and the depolarizer are cations, besides the blocking effect of the covered electrode surface an electrostatic influence (ψ_1 effect) is displayed[18].

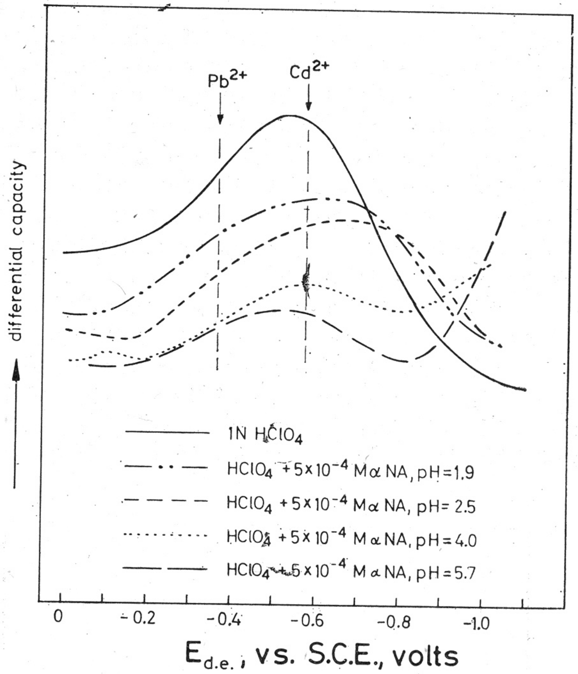


Fig. 14. Differential capacity curves of 1 N $HClO_4$ and of $HClO_4$ solutions pH 1.9—5.7 with addition of α-naphthylamine (DME).

The change of the inhibition of cadmium and lead electrode reactions with the change of *p*H in the α-naphthylamine solutions is still more interesting. The inhibitory effect reaches a maximum in the range of equivalence point at *p*H 4.5 for both cations. With a further increase of *p*H the inhibition decreases abruptly, so it is evident that RNH_3^+ ions inhibit considerably more than the neutral RNH_2 molecules. However, the inhibitory effect of α-naphthylaminium cations are strongly influenced by the concentration of hydrogen

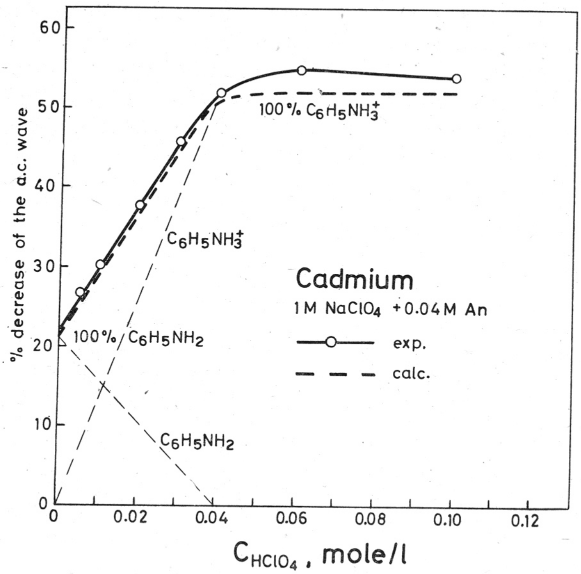


Fig. 15. Experimental and calculated inhibition curves of cadmium in $HClO_4$ solutions of aniline.

ions, this being probably in connection with a change of structure of the electric double-layer. The difference in the behaviour of aniline and α-naphthylamine points to the necessity of further systematic investigations in that field.

The influence of chloride ion on the rate of inhibited electrode processes has recently been studied by Loshkarev, Kriukova, Loshkarev, and Diachenko[19] and such investigations have lately been extended also to other deformable anions by Kůta and Smoler[20]. It has been found that the rate of electrode processes increases in the presence of halide ion. The accelerating effect is mainly the result of a decrease in the activation energy[19] by the bridge formation between the deformable anion and the depolarizer cation, whereby the electron transfer is facilitated[19,20]. It is probable that the accelerating action increases with the specific adsorption of intermediate complexes[20]. The relation between the electrode reaction rate constant and the deformable anion concentration depends on the inhibitor and depolarizer used[20]. Our investigations of the influence of chloride ion on the rate of the inhibited a. c. polarographic electrode process of cadmium in 1*N* $HClO_4$ (Fig. 8) are in accordance with the quoted investigations. However, it seems that the accelerating effect, i. e. the per cent increase of the inhibited cadmium a. c. wave, does not depend on the nature of investigated amines. The concentration of about 0.1 *M* of chloride eliminated the inhibiting action of all investigated amines almost completely. The linear relation between the accelerating effect and the chloride concentration is in accordance with the cited investigations[20].

The obtained extent of inhibition in the sequence *n*-butylamine $<$ pyridine $<$ aniline $<$ triethylamine $<$ *o*-methylpyridine $<$ *o*-toluidine $<$ 2,3-dimethylaniline $<$ 2,6-dimethylaniline $<$ quinoline $<$ α-naphthylamine corresponds to the increasing inhibition efficiency as corrosion inhibitors[13,1]. The position of amines with a substituted electron-donating methyl group in this sequence is in accordance with electron density theory of inhibition[21]. It can be concluded, therefore, that a. c. polarographic investigations of the inhibitory effect of amines on the electrode processes of cadmium and/or lead can serve as a very appropriate method for determining the effective range of concentration of amines as corrosion inhibitors.

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IZVOD

Inhibitorsko djelovanje amina na polarografske procese u kiseloj otopini. II. Istraživanje polarografskom metodom izmjenične struje

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Proučavan je utjecaj nekih amina na polarografske valove izmjenične struje kadmiuma i olova. Inhibitorsko djelovanje amina u 1 *N* $HClO_4$, koje se očituje u sniženju polarografskoga vala izmjenične struje, raste u nizu: *n*-butilamin $<$ $<$ piridin $<$ anilin $<$ trietilamin $<$ *o*-metilpiridin $<$ *o*-toluidin $<$ 2,3-dimetilanilin $<$ 2,6-dimetilanilin $<$ kinolin $<$ α-naftilamin. Kako u istom nizu raste i sposobnost inhibiranja procesa korozije, može se ova metoda vrlo dobro primijeniti za ocjenji-

vanje inhibitorskih sposobnosti amina u kiselim otopinama. Nadalje je nađeno da se inhibitorsko djelovanje ispitivanih amina u 1 *N* H_2SO_4 malo razlikuje od onog u 1 *N* $HClO_4$, dok je znatno izrazitije u 1 *N* H_3PO_4. Studiran je i utjecaj pH otopine na proces inhibiranja. Nađeno je da aminium ioni RNH_3^+ jače inhibiraju od molekula amina RNH_2. Konačno je ispitan i utjecaj klorid-iona na inhibirani elektrodni proces. Ustanovljeno je, da klorid-ioni ubrzavaju inhibirani elektrodni proces i da postoji linearni odnos između efekta ubrzavanja i koncentracije klorid-iona.

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