Inhibitory Effect of Amines on Polarographic Processes in Acid Solution. I. D. C. Polarographic and Oscillopolarographic Investigation

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The influence of some amines as capillary active substances and as corrosion inhibitors in acid solution was studied by the conventional d. c. polarographic method and oscillopolarographically. The electrode processes of thallium, cadmium, lead, zinc and bismuth have served as indicators of the inhibitor efficiency. The inhibition of the electrode processes, resulting in a decrease of the limiting current and in the shift of the half-wave potential toward more negative values as well as in a deminution of the corresponding incision on the oscillopolarographic curve, was found to increase, generally, in the order: methylamine $<$ *n*-butylamine $<$ pyridine $<$ $<$ aniline $<$ quinoline $<$ α-naphthylamine. Since the same sequence was found for the inhibition of corrosion processes, it can be concluded that the cited effects are suited for the evaluation of the inhibiting efficiency of amines in acid solutions.

Today organic substances are videly used for the inhibition of corrosion processes and especially to inhibit the attack of the acid on the metal during acid pickling[1]. In addition such inhibitors kinetically change the cathodic and anodic processes and are important additives in technological processes of metal deposition. Among numerous organic compounds the amines and heterocyclic compounds of nitrogen are of special interest. Their effectivenes as corrosion inhibitors is a result of their adsorptive properties[2-6]. The great practical importance of amines as inhibitors has caused an intensive investigation of their inhibiting properties by various methods, among others the polarographic method[5,7].

By adsorption of the capillary active substance on the surface of the mercury electrode[8], the electrochemical process of reduction (or oxidation) of a certain depolarizer is influenced kinetically[9]. In spite of the fact that polarographic and corrosion processes are not identical, a parallelism of the effects exists, since in both cases the adsorbed inhibitor retards the electrochemical reaction[10].

This paper presents the results of investigations of the influence of some amines as surface active substances on polarographic electrode processes of some metallic cations by the conventional d. c. polarographic method and by the oscillopolarographic method.

The theory of the influence of the surface active substances on polarographic currents and the polarographic wave was given by Koryta, Koutecký, Kuta and Weber[11-14]. The decrease of the polarographic wave is due to the

blocking of the surface of the dropping mercury electrode by the adsorbed film of the inhibitor. In the case of a reversible electrode process only the decrease of the polarographic wave with the increase of the inhibitor concentration occurs[11]. When the electrode reaction is polarographically irreversible, the decrease of the polarographic wave is also a function of the kinetic factor, *i. e.* a shift of the polarographic wave to more negative potentials also takes place[14].

If the inhibitor and depolarizer are ions, besides the blocking affect of the covered electrode surface an electrostatic influence (ψ_1 effect) is displayed[14,15]. Therefore, by the adsorption of the cation of the surface active substance the wave of the depolarizer cation is shifted to more negative potentials than in the presence of an uncharged inhibitor.

When the electrode reaction takes place not only on the free surface but on the covered surface of the electrode as well, two waves can appear[14].

In the oscillopolarographic investigation the electrode process was followed by way of the function $dE/dt = f(E)$[16]. The electrode process of the depolarizer results in an incision in the cathodic and anodic part of the elliptic curve. An inhibited electrode reaction is revealed by a decrease of the cathodic incision, or by a deformation of the sharp reversible incision into an irreversible kinetic incision which is L shaped. At the same time the cathodic incision can be shifted to more negative values, in which case asymmetrical anodic and cathodic incisions are observed. Since the anodic process is taking place in the metallic phase, the inhibitor has no direct influence on the anodic incision. However, the retardation of the cathodic process, *i. e.* the formation of less amalgam is causing a decrease of the anodic incision. This effect was especially pronounced on $dE/dt = f(E)$ curves obtained with the streaming mercury electrode with which the solution is in contact only for a very short period. With the streaming electrode therefore the retardation of the electrode reaction can be evaluated from both the anodic and the cathodic incision.

<div align="center">EXPERIMENTAL</div>

The measurements of the polarographic currents were performed on the polarographs: Heyrovský Model V-301 (Kovo), Leybold Polarograph Model 35 and Manual polarograph B MK II (The Electrochemical Laboratories). The potential drop across the potentiometer of the polarograph was as low as 500 mv, which was attained by the switching of corresponding resistances in front of and behind the potentiometer. In this way a maximum accuracy of the half-wave potential determinations of ± 2 mV was achieved. The polarographic cell and other equipment did not differ from that described in a previous paper[17]. All half-wave potentials (corrected to the voltage drop iR) are given with respect to the calomel electrode with a saturated solution of sodium chloride. The limiting or diffusion current was measured at the half-wave potential. The characteristics of capillaries used: $m =$ from 1.52 to 2.29 mg./sec. and $t =$ from 3.52 to 5.40 sec. All measurements were carried out under constant temperature of $25 ± 0.1^0$ C.

For the preparation of solutions an analytical-grade 70⁰/₀ perchloric acid (C. Erba) was used. The solutions of metallic perchlorates were prepared by dissolving corresponding oxides in perchloric acid. The amines were dissolved in an equivalent amount of perchloric acid. They had the following purity: methylamine *purris.* grade, *n*-butylamine *puriss.* grade, aniline analytical-grade, α-naphthylamine analytical-grade, pyridine analytical-grade and quinoline *purum* grade, all of the firm Fluka. Redistilled water and redistilled mercury was used.

Solutions used for polarographic measurements contained perchloric acid in 1 *M* concentration, whereas the concentration of cadmium, lead, and bismuth perchlorate was 0.4 m*M*.

The oscillopolarographic measurements were performed with the Polaroscope P 576, Križik[16]. Pictures of the oscillograms of the functions dE/dt = f (E) were taken with a camera Exacta Varex II A with a wide-angle lens Flektogon. The film was Eastman Tri X (27⁰ DIN). The exposure time was $1/50$ of a second when the streaming electrode was used, and with the dropping mercury electrode the shutter was open all the time during the growth of the mercury drop. For the measurement of the relative depth of the incision, i. e. the ratio of the incision depth and the value of dE/dt for the same solution but without the depolarizer (h/h$_0$), an enlarger was used. The precision of such measurements was within ± 10⁰/₀.

A modified electrolytic cell after Györbiró, Poós, and Proszt[16] was used. It enabled the maintenance of a constant level of the liquid. A pool of mercury on the bottom of the polarographic vessel served as reference electrode.

The measurements were carried out in solutions containing 1 mol/l. of HClO$_4$, metal perchlorates in a concentration of 2 mM for cadmium and lead and of 0.4 mM for thalium, zinc and bismuth. The amines were added in step-wise increasing concentrations from 0.1 mM to the maximum concentration which was possible with respect to the solubility of the amines.

The metal amalgams were obtained by direct dissolution of the metal in mercury, which was done in a stream of pure nitrogen. All parts of the amalgam electrode were of glass, in order to prevent a change of the amalgam concentration caused by the use of plastic or rubber tubing.

RESULTS

Of the investigated amines none has any influence on the electrode process of monovalent thallium. For the rest of the investigated cations almost no
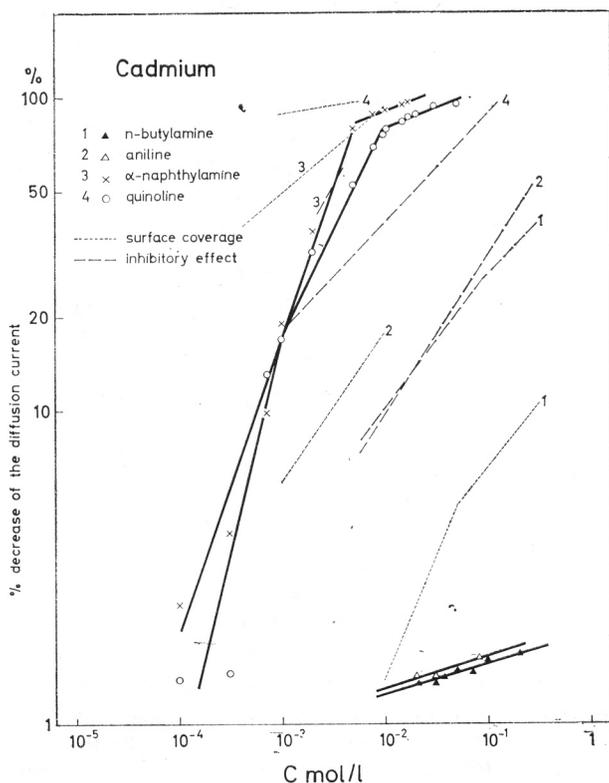

Fig. 1. The decrease of the polarographic wave of cadmium as a function of the amine concentration. In comparison with the surface coverage on Hg, measured in 0.1 N HCl at the e. c. m.[21] (dotted lines) and in comparison with the corrosion inhibiting efficiency[22] (dashed lines).

influence was observed with methylamine even in concentrations as high as 0.50 M.

Polarographic Measurements

With polarographically reversible electrode processes of cadmium and lead the decrease of the diffusion current was determined, *i. e.* the relation i_d/i_d^0 where i_d is the diffusion current in the presence of the inhibitor and i_d^0 is the diffusion current in the absence of the inhibitor. For the polarographically irreversible electrode reaction of bismuth besides the decrease of the diffusion current (i_d/i_d^0) the shift of the half-wave potential ($\Delta E_{1/2}$) was also determined.

The results of the measurements are represented in Figs. 1—4 by plotting the cited values against the inhibitor concentration.
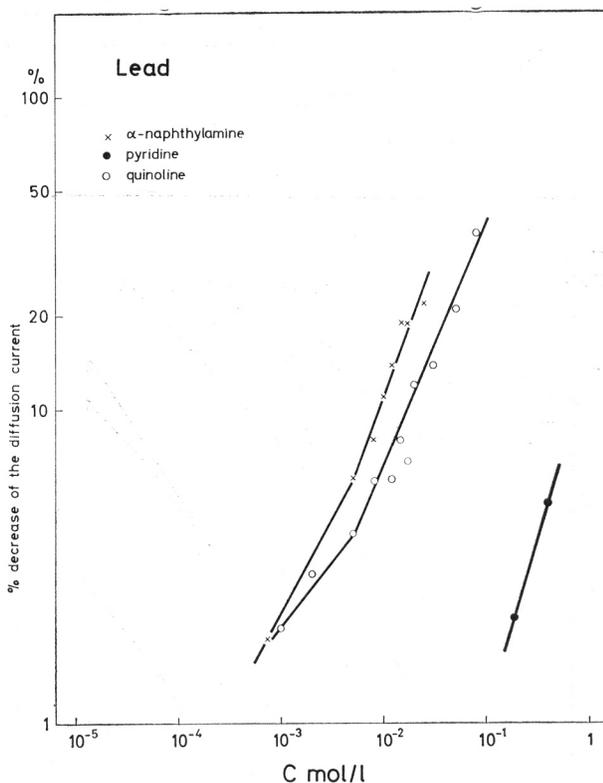
Fig. 2. The decrease of the polarographic wave of lead as a function of the amine concentration.

n-Butylamine and aniline, practically, do not diminish the polarographic waves of lead and bismuth, whereas the cadmium wave is slightly decreased. Pyridine decreases the lead wave only slightly, whereas it affects the bismuth wave considerably more (decrease to 10%). In the case of cadmium, pyridine in higher concentrations ($\geqslant 10^{-1}$ mol/l.) causes the splitting of the wave in two waves. The first wave has a slope corresponding to the polarographically

reversible electrode process of cadmium. Accordingly, the first wave corresponds to the reduction of the cadmium ion on the free and the second one on the covered surface of the dropping mercury electrode[14].

Oscillopolarographic Measurements

The inhibitory effect of the five cited amines is especially pronounced for the oscillopolarographically reversible electrode process of cadmium. Figs. 5—10 show typical oscillopolarograms obtained with a streaming electrode in 1 *M* perchloric acid with no depolarizer, and with cadmium as depolarizer without and with the addition of some of the investigated amines. Small concentrations of amines reduce the depth of the cathodic incision and change its form into an L shape (Fig. 7). Greater amounts of amines shift the decreased and L-shaped incision to more negative potentials (Fig. 8) or else the incision
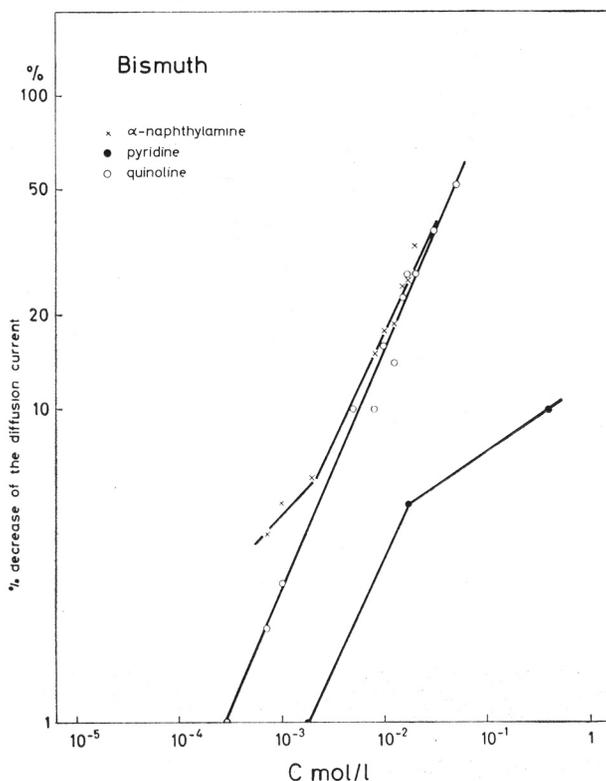
Fig. 3. The decrease of the polarographic wave of bismuth as a function of the amine concentration.

disappears. In the presence of small amounts of quinoline an additional cathodic incision is formed by catalytic reduction of hydrogen (Fig. 9)[18], while with higher concentrations of quinoline the incision depth grows to such an extent that the curve is finished at this point. At the same time the electrode process of cadmium is completely inhibited (Fig. 10).

The depth, the shape and the position of the anodic incision is not changed when the dropping mercury electrode is used, whereas with the streaming electrode the anodic incision is decreased (Figs. 8 and 10).

With lead, which gives also oscillopolarographically reversible electrode process, an analogous effect can be observed which, however, is smaller in comparison with that observed for cadmium.

Zinc is not very suitable for the evaluation of inhibition effects since it gives an oscillopolarographically irreversible process with incisions at the end of the curve.
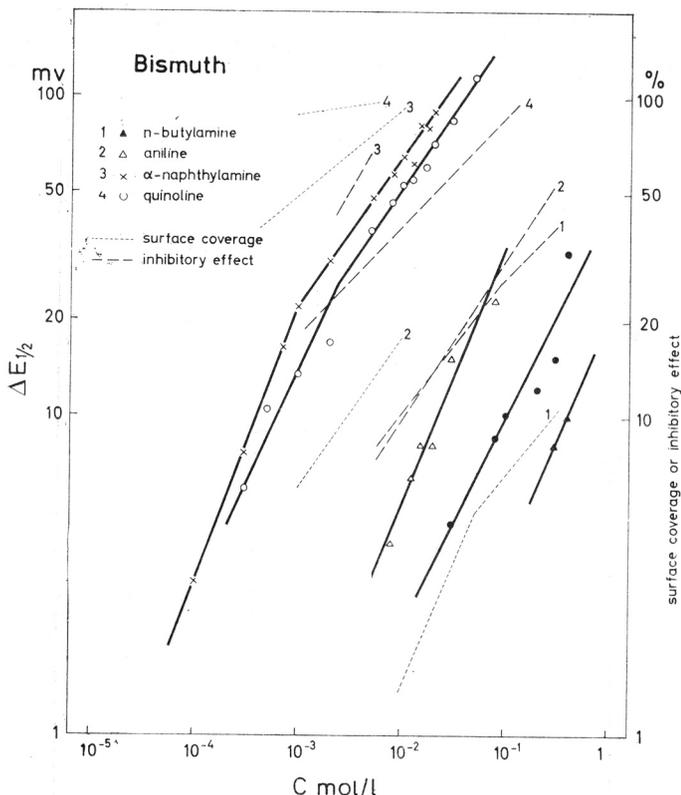
Fig. 4. **The shift of the half-wave potential of** bismuth to more negative potentials as a function **of the amine concentration. In comparison with** % of surface coverage on Hg[21] (dotted lines) **and corrosion inhibiting efficiency**[22] (dashed lines).

The oscillopolarographic behaviour of bismuth in perchloric acid solutions is interesting when the streaming electrode is used and when small current intensities are applied (0.3 mA). Thereby symetrical shallow incisions are formed in the cathodic and anodic part of the oscillogram (Fig. 11). By an increase of the current intensity (1.3 mA) two new symmetrical incisions are formed at more positive potentials (Fig. 12). An analogous, but only anodic incision is formed when the dropping electrode is used even with a small current intensity (Fig. 13). In this case no anodic incision at more negative potentials can be observed. The same position of incisions is observed with
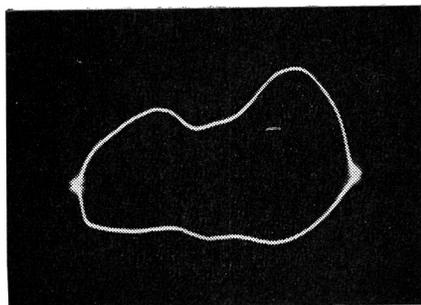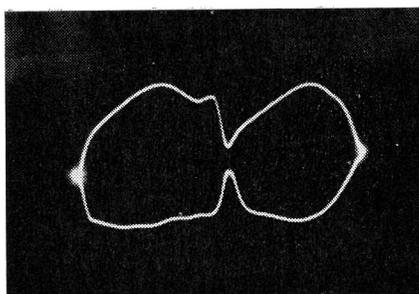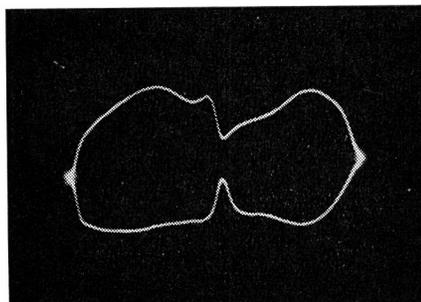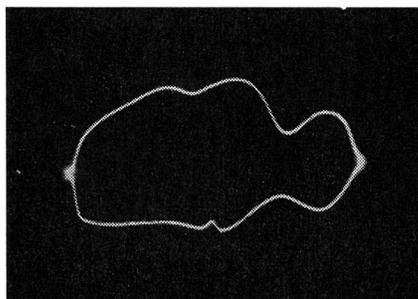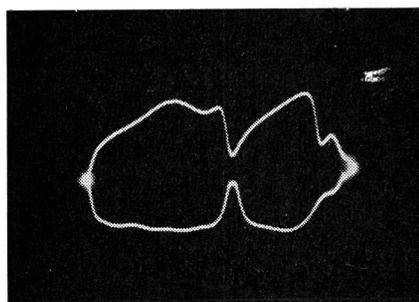
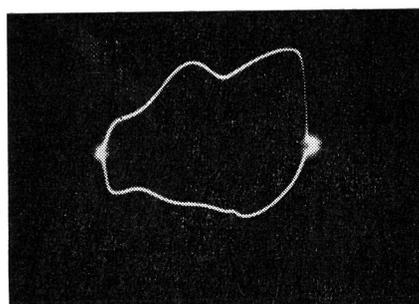Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Oscillopolarographic curves in perchloric acid with varying concentrations of amines. Fig. 5: 1 M HClO$_4$. Fig. 6: 1 M HClO$_4$ + 2 mM Cd^{2+}. Fig. 7: Same with 0.05 M n-butylamine. Fig. 8: Same with 0.4 M n-butylamine. Fig. 9: Same with 0.3 mM quinoline. Fig. 10: Same with 0.015 M quinoline.
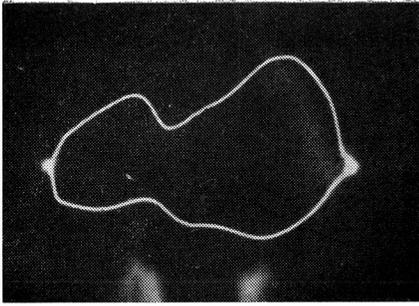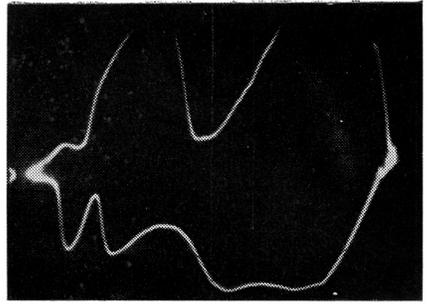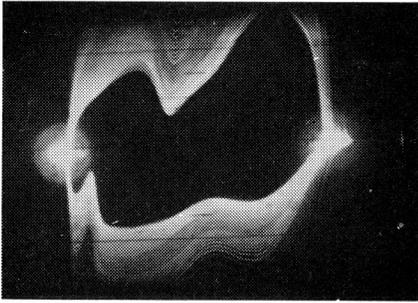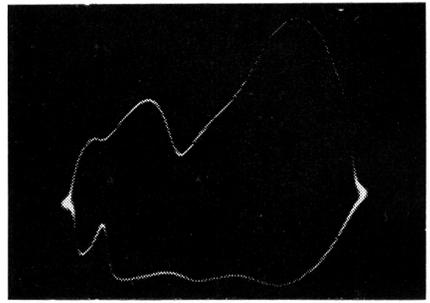
Fig. 11

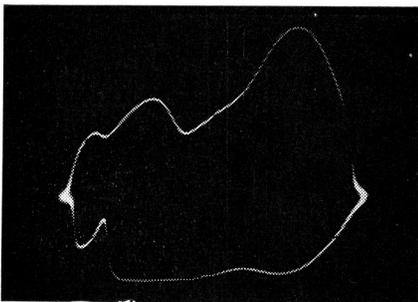Fig. 12

Fig. 13

Fig. 14

Fig. 15

Fig. 16

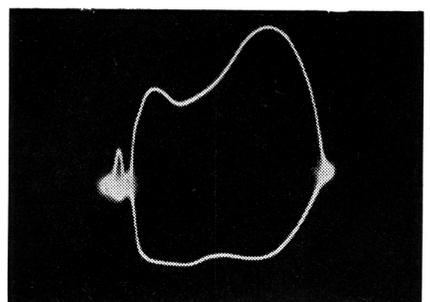Oscillopolarographic curves of bismuth in 1 M perchloric acid. Fig. 11: 0.4 mM Bi^{3+} (0.3 mA). Fig. 12: 0.4 mM Bi^{3+} (1.3 mA). Fig. 13: 0.4 mM Bi^{3+} (dropping electrode). Fig. 14: 0.4 mM bismuth amalgam electrode. Fig. 15: 0.4 mM bismuth amalgam electrode in 0.4 mM Bi^{3+}. Fig. 16: 0.4 mM Bi^{3+} + 0.02 M HCl.

a bismuth amalgam electrode in pure perchloric acid even with small current intensities (Fig. 14). When bismuth is present both in the amalgam and in the solution, only an increase of the shallow secondary cathodic and anodic incision can be observed since bismuth in solution does not participate in the formation of the primary incisions (Fig. 15).

From such behaviour it could be concluded that the incisions of bismuth at more positive and negative potentials are of different origin, and that the more positive incisions can be formed only with a sufficient concentration of
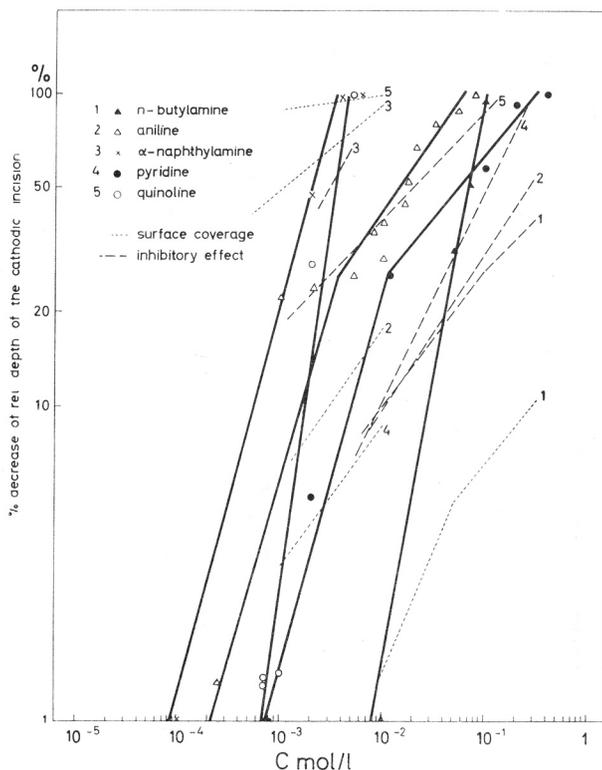

Fig. 17: Decrease of depth of cathodic incision of cadmium, surface coverage on Hg (in 0.1 N HCl at e. c. m.)[21] and corrosion inhibiting efficiency [22] as functions of concentration of amines.

bismuth in the amalgam. The incisions at more negative potentials could be ascribed to a markedly irreversible electrode process or to an adsorption--desorption process, because a reversible process, such as observed in a chloride medium[19,20], gives symetrical incisions at more positive potentials (Fig. 16). The inhibitory effect observed on the primary incisions was non-existent for n-butylamine and aniline, a small one for pyridine and a somewhat more pronounced for α-naphthylamine and quinoline. The effect was however decidedly smaller than with cadmium.

DISCUSSION

Recent investigations of the adsorption of amines at the mercury solution interface have shown[21] that the inhibiting properties of amines are in the first

place a consequence of the surface coverage by the adsorbed film. The abillity of electrosorption of amines is increasing with molecular dimensions[21] and with a diminution of their solubility[8,21]. The greater efficiency of aromatic amines is a result of their planar orientation in the adsorbed film and a π-electronic interaction of the conjugated double bonds of the aromatic nucleus with the metal[21]. The strenght of the adsorption is increasing with the number of conjugated double bonds. A parallelism was found between the inhibition efficiency of the acid attack on iron and the surface coverage of the mercury
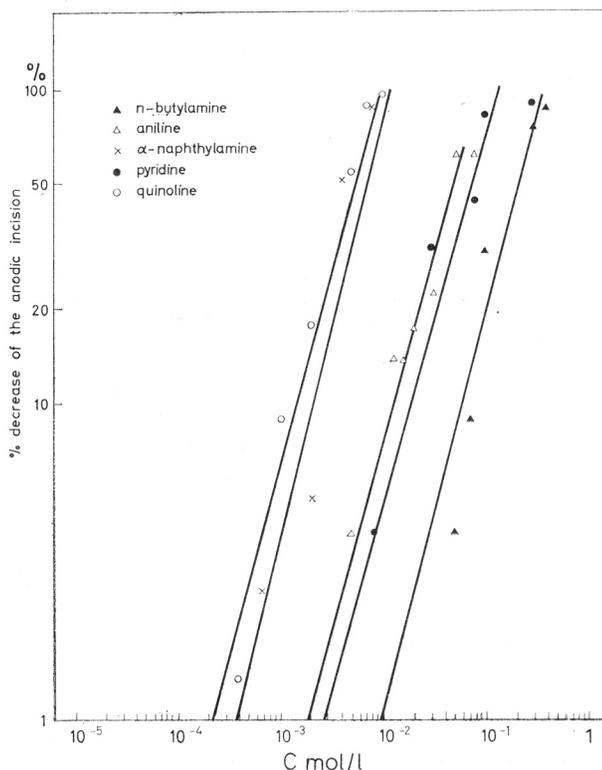

Fig. 18: Decrease of anodic incision of cadmium as function of concentration of amines.

electrode[21]. This polarographic investigation is in agreement with the cited results.

Polarographic Investigation

Strong surface active amines, α-naphthylamine and quinoline, diminish considerably the polarographic waves of cadmium, lead and bismuth in the following order: cadmium > bismuth > lead. α-Naphthylamine is a somewhat stronger inhibitor than quinoline. α-Naphthylamine and quinoline exhibit a considerably greater influence on the limiting current of the indicator ions used, and especially that of cadmium, that the other amines which were used. This fact is in agreement with their well pronounced ability of surface covering due to the interaction of π-electrons of the conjugated bonds of

the aromatic nuclei[21]. The inhibition of the electrode reaction of cadmium by α-naphthylamine and quinoline is in accordance with their efficiency as inhibitors of iron corrosion[22].

Accordingly, the decrease of the polarographic wave of cadmium may be taken as a measure of the inhibiting effect of amines on the corrosion of iron in acid solutions. This method is, however, less suitable than the oscillopolarographic method, because the latter makes possible a better differentiation of
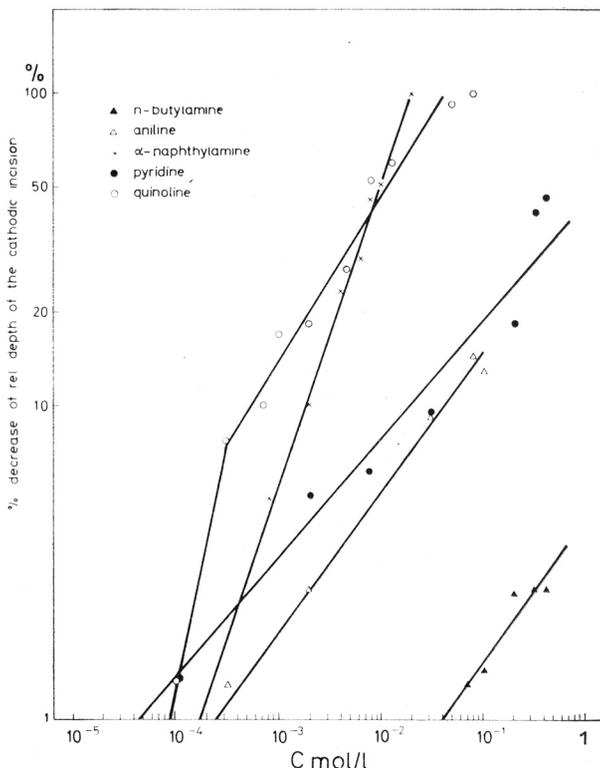

Fig. 19: Decrease of depth of cathodic incision of lead as function of concentration of amines.

the inhibitory efficiency even with less surface active amines (n-butylamine, aniline, pyridine).

The inhibiting effect of polarographically irreversible electrode process of bismuth, which results in the shift of the half-wave potential to more negative values with the increase of amine concentration, increases in the order (Fig. 4): n-butylamine < pyridine < aniline < quinoline < α-naphthylamine. As the same order (except for pyridine and aniline) is valid for the inhibiting efficiency of iron corrosion, this effect of the shift of the half-wave potential of bismuth is better suited for determining the effective range of concentration of the amine as corrosion inhibitor.

Oscillopolarographic Investigation

In Figs. 17 and 18 it can be seen that the inhibition efficiency, displayed as a diminution of the relative depth of the incision (h/h_0) on the curve

$dE/dt = f(E)$, goes parallelly to the percent of surface coverage: n-butylamine $<$ $<$ pyridine $<$ aniline $<$ quinoline $<$ α-naphthylamine. The percent decrease of the incision depth is in very good agrement with the inhibition efficiency for mild steel (in 1 M H_2SO_4)[1,21,22], except for aniline (Fig. 17). The percent decrease of the incision depth is generally greater than the inhibition efficiency for the same concentration of amines. The difference is especially marked for aniline.
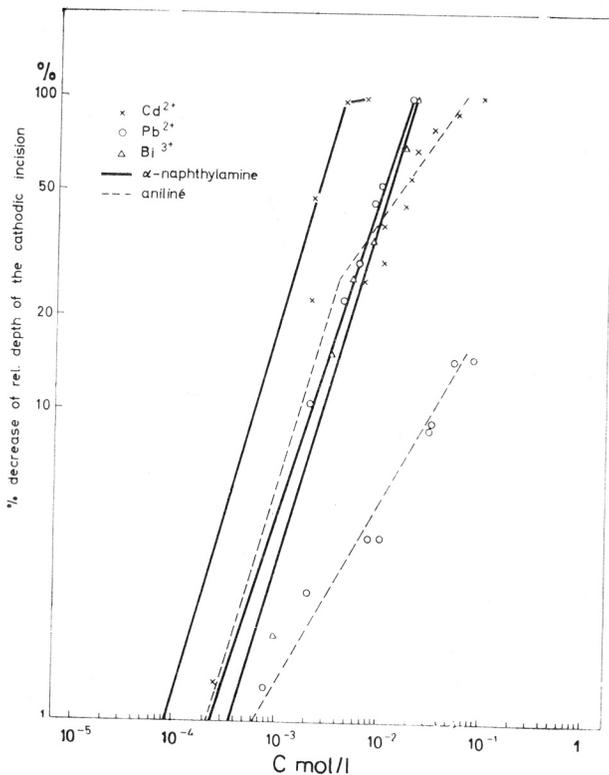

Fig. 20: Decrease of depth of cathodic incision of cadmium, lead and bismuth as function of concentration of amines.

The inhibition of the electrode reaction of lead (Fig. 19) with the investigated amines is less intensive than for cadmium. Aniline is a weaker inhibitor than pyridine. The same is true for the electrode reaction of bismuth.

It can be concluded, therefore, that oscillopolarographic investigations of the inhibitory effect of amines on the electrode process of a suitable indicator cation can serve as an appropriate method for determining the effective range of concentration of amines as corrosion inhibitors of mild steel.

From Fig. 20 it can be seen that the decrease of the incision with the same concentration of amine is considerably greater for cadmium than for lead and bismuth. This is in accordance with the fact that the amines are preferably electrosorbed as RNH_3^+ ions from acid solutions[21]. Accordingly, due to smaller surface coverage of the electrode at more positive potentials, a weaker influence is observed with cations which have depolarizing potentials

at the positive part of the electrocapillary curve (in 1 N HClO$_4$ the potential of the e. c. m. is -0.510 V, and the relevant half-wave potentials are for cadmium -0.562 V, lead -0.378 V, and bismuth -0.050 V vs. S. C. E.)[23]. As a consequence the incisions of lead and bismuth are decreased only by α-naphthylamine and quinoline, which can be adsorbed by π-electronic interactions of conjugated double bonds with the surface of mercury at potentials on the positive side of the electrocapillary curve.

The investigated amines are inhibiting only the two and three-electron processes of cadmium, lead, zinc and bismuth, whereas for thallium no effect can be observed. This would be expected on the basis of the theory given by J. Heyrovský for the mechanism of the retardation of electrode reactions[24].

REFERENCES

1. H. H. Uhlig, *Corrosion Handbook*, J. Wiley and Sons, New York, 1948.
2. N. Hackerman and A. C. Makrides, *Ind. Eng. Chem.* **46** (1954) 523.
3. C. P. De, *Nature* **180** (1957) 803.
4. C. A. Mann, *J. Electrochem. Soc.* **69** (1936) 115.
5. C. N. Reilley and W. Stumm, *Progress in Polarography*, Vol. I, p. 81, edited by P. Zuman. Interscience Publishers, Inc., New York, 1962.
6. A. N. Frumkin and B. B. Damaskin, *Modern Aspects of Electrochemistry*, No. 3, p. 149, edited by J. O'M. Bockris and B. E. Conway, Butterworths, London, 1964.
7. H. W. Nürnberg and M. von Stackelberg, *J. Electroanal. Chem.* **4** (1962) 1.
8. E. Gileadi, *J. Electroanal. Chem.* **11** (1966) 137.
9. J. Heyrovský and J. Kuta, *Zaklady polarografie*, Nakladatelstvi Československe Akademie, Praha, 1962.
10. (a) L. Horner and F. Röttger, *Korrosion* 16, p. 57. Verlag Chemie, Weinheim, 1963.
    (b) L. Holleck and B. Kastening, *ibid.*, p. 29.
11. J. Koryta, *Collection Czech. Chem. Commun.* **18** (1953) 206.
12. J. Weber, J. Koutecký, and J. Koryta, *Z. Electrochem.* **63** (1959) 583.
13. J. Koutecký and J. Weber, *Collection Czech. Chem. Commun.* **25** (1960) 1423.
14. J. Kuta, J. E. Weber, and J. Koutecký, *ibid.* **25** (1960) 2377.
15. I. M. Kolthoff and Y. Okinaka, *J. Am. Chem. Soc.* **81** (1959) 2296.
16. J. Heyrovský and R. Kalvoda, *Oszillographische Polarographie mit Wechselstrom*, Akademie Verlag, Berlin, 1960.
17. I. Filipović, A. Bujak, H. Marač, R. Novak, and V. Vukičević, *Croat. Chem. Acta* **32** (1960) 219.
18. B. Lovreček and T. Jukić-Markušić, *Croat. Chem. Acta* **28** (1956) 255.
19. (a) J. Heyrovský, *Discusions Faraday Soc.* **1** (1947) 212.
    (b) K. Itsuki and M. Nagao, *Japan Analyst* **8** (1959) 800.
    (c) D. Weiss, *J. Electroanal. Chem.* **5** (1963) 62.
20. I. Filipović, *Croat. Chem. Acta* **23** (1951) 159.
21. (a) E. Blomgren and J. O'M. Bockris, *J. Phys. Chem.* **63** (1959) 147.
    (b) E. Blomgren, J. O'M. Bockris, and C. Jesch, *ibid.* **65** (1961) 2000.
    (c) S. L. Djatkina and B. B. Damaskin, *Elektrohimija* **2** (1966) 1340.
22. C. A. Mann, B. E. Lauer, and C. T. Hultin, *Ind. Eng. Chem.* **28** (1936) 159, 1048.
23. Unpublished results from this laboratory.
24. (a) J. Heyrovský, *Collection Czech. Chem. Commun.* **19** (1954) 58.
    (b) J. Heyrovský, F. Šorm, and J. Forejt, *ibid.* **12** (1947) 11.

IZVOD

Inhibitorsko djelovanje amina na polarografske elektrodne procese u kiseloj otopini. I. Polarografsko i oscilopolarografsko istraživanje

I. Filipović, A. Medved i I. Piljac

Studiran je utjecaj nekih amina na polarografske valove taliuma, kadmiuma, olova, cinka i bismuta u 1 N otopini perklorne kiseline. Određeno je sniženje granične struje kadmiuma, olova i bismuta kao i pomak poluvalnog potencijala bismuta prema negativnijim vrijednostima potencijala. Određeno je i smanjenje dubine ureza kadmiuma, olova i bismuta na oscilopolarografskoj krivulji dE/dt = f (E). Nađeno je da ovi efekti uglavnom rastu u nizu: metilamin < n-butilamin < piridin < anilin < < kinolin < α-naftilamin. Kako u istom nizu raste i sposobnost inhibiranja procesa korozije, mogu navedeni efekti poslužiti za ocjenjivanje inhibitorske sposobnosti amina u kiselim otopinama.

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