

# Electrode process of deposition and dissolution of the Al—Pb binary system in an organic electrolyte

## I. Lead(II) bromide and aluminium(III) bromide reduction in ethylbenzene electrolyte

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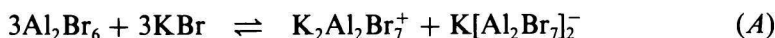
The deposition reactions of metallic lead and aluminium from  $\text{AlBr}_3 + \text{PbBr}_2 + \text{KBr}$  solution in ethylbenzene have been studied using cyclic voltammetry and chronopotentiometry as methods. The reduction of  $\text{AlBr}_3$  in the absence of  $\text{PbBr}_2$  proceeds nearly reversibly at zero electrode potential vs. aluminium electrode. The addition of  $\text{PbBr}_2$  causes negative shift of the aluminium deposition potential of about 50—70 mV. The difference between lead and aluminium deposition potentials is approximately 300 mV contrary to 1400 mV in aqueous solution. This fact is very important from the point of view of simultaneous deposition of both metals.  $\text{PbBr}_2$  is reduced in two steps. The reduction process is diffusion-controlled at sufficiently high scan rate values. A slow catalytic chemical reaction proceeding between both electrode reduction steps has been observed at lower scan rate values leading to the decrease of voltammetric current. Possible explanations of this effect are discussed.

С использованием методов циклической вольтамперии и хронопотенциометрии изучены реакции осаждения металлических свинца и алюминия из раствора смеси  $\text{AlBr}_3 + \text{PbBr}_2 + \text{KBr}$  в этилбензоле. Восстановление  $\text{AlBr}_3$  в отсутствие  $\text{PbBr}_2$  протекает почти обратимо при нулевом электродном потенциале по сравнению с алюминиевым электродом. Добавление  $\text{PbBr}_2$  вызывает уменьшение потенциала осаждения алюминия на 50—70 мВ. Разница между потенциалами осаждения свинца и алюминия в данном случае приблизительно равна 300 мВ по сравнению с 1400 мВ в водном растворе. Этот факт особенно важен с точки зрения одновременного осаждения обоих металлов. Восстановление  $\text{PbBr}_2$  протекает двухстадийно. Процесс восстановления управляется процессом диффузии при достаточно высоких значениях скорости сканирования. При более низких скоростях сканирования наблюдалась медленная каталитическая химическая реакция, про-

текающая между двумя стадиями электродного восстановления. Эта реакция вела к уменьшению величины вольтамметрического тока. Обсуждаются возможные варианты объяснения этого эффекта.

Two-component Al—Pb metal coating, employable also in the sliding bearings industry, may electrochemically be deposited only from electrolytes suitable for the deposition of more negative aluminium. Aqueous solutions cannot be used, as it is commonly known, only melts and organic electrolytes. From the organic electrolytes, those based on ether-type solvent as diethyl ether, tetrahydrofuran [1—4] or on aromatic hydrocarbon-type solvent as benzene, toluene, xylene, ethylbenzene, *etc.* [5—8], are the most suitable. The experiments carried out in our laboratory have shown that for two-component Al—Pb coating deposition the aromatic hydrocarbons based electrolyte is better since it enables application of broader concentration range of lead in the solution and, consequently, in the coating as well [9, 10].

Dimeric molecules  $\text{Al}_2\text{Br}_6$ , undissociated in totally dry solvent, are present in an  $\text{AlBr}_3$  solution in aromatic hydrocarbons [7, 11]. Ions are formed only with addition of further components such as potassium bromide [6], hydrobromic acid [5, 7] or quaternary ammonium bromide [12] to the solution. Basic electrolyte used in the present work contained potassium bromide; ionization in the used concentration range of both  $\text{AlBr}_3$  and  $\text{KBr}$  proceeds as follows [13]



Both viscosity and cryoscopic measurements have shown that ionic aggregates are formed by the particles at the right-hand side of eqn (A). The conductance of such solutions is relatively high since the transfer of charge is realized, similarly as in aqueous solutions of strong mineral acids, by the so-called "hopping mechanism", *i.e.* by exchange of charged particles between the aggregates in the direction of electric field [13]. So the conductivity of a solution containing 2.5 to 3.0 mol dm<sup>-3</sup>  $\text{AlBr}_3$  and 1.0 to 1.5 mol dm<sup>-3</sup>  $\text{KBr}$  ranges between 5 to 9 mS cm<sup>-1</sup>.

The present paper deals with the study of cathodic deposition of aluminium and lead from the above-described ethylbenzene electrolyte. Similar subject is treated in the paper [14] where cyclic voltammetric behaviour of Pb and Sn in the same electrolyte on a Pt electrode is described.

### Experimental

Cyclic voltammetry (CV) and chronopotentiometry (ChP) were used for the study. The three-electrode arrangement consisted of a working stainless-steel electrode with a surface area 0.102 cm<sup>2</sup> and aluminium wire counter and reference electrodes. All experiments were carried out under air- and waterfree conditions in dry argon atmosphere on the GWP 673 Polarograph (GDR).

Ethylbenzene (ETB) was dried by storing over metallic sodium for several days followed by repeated reflux and distillation from metallic sodium or potassium. Water-free  $\text{AlBr}_3$  from Reakhim (USSR) was used without further purification.  $\text{KBr}$  was dried by melting at  $400^\circ\text{C}$ .  $\text{PbBr}_2$  was dried at  $100^\circ\text{C}$  in a vacuum oven for 48 h. Electrolyte was prepared and stored in dry argon atmosphere.

### Results and discussion

CV record of the basic electrolyte  $\text{AlBr}_3 + \text{KBr}$  is shown in Fig. 1, curve 1.

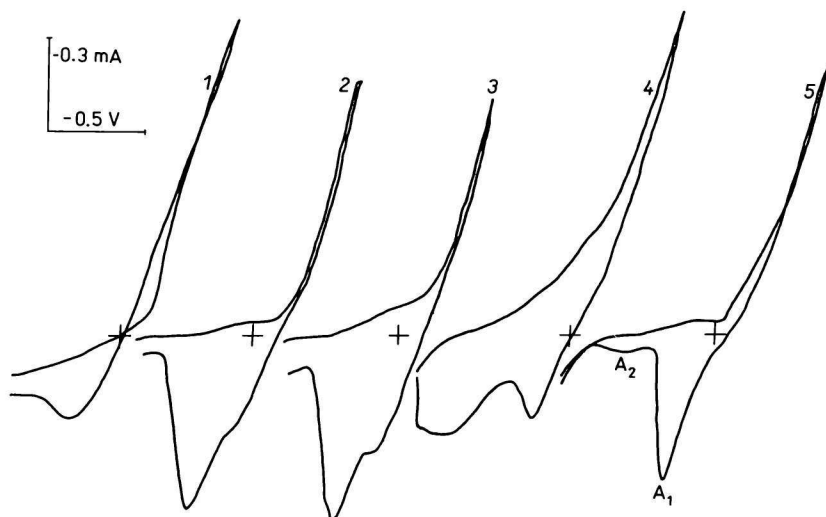


Fig. 1. Voltammetric record of the electrode reactions in the  $\text{PbBr}_2 + \text{AlBr}_3 + \text{KBr}$  electrolyte in ethylbenzene.  $c(\text{AlBr}_3) = 1.92 \text{ mol dm}^{-3}$ ,  $c(\text{KBr}) = 0.80 \text{ mol dm}^{-3}$ . Concentration of  $\text{PbBr}_2$ : 1.  $0 \text{ mol dm}^{-3}$ ; 2.  $1.69 \times 10^{-3} \text{ mol dm}^{-3}$ ; 3.  $2.53 \times 10^{-3} \text{ mol dm}^{-3}$ ; 4. and 5.  $5.1 \times 10^{-3} \text{ mol dm}^{-3}$ . Sweep rate: 1.—4.  $0.25 \text{ V s}^{-1}$ ; 5.  $0.0166 \text{ V s}^{-1}$ .

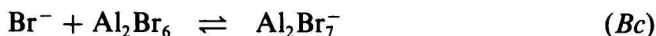
Both deposition and dissolution of Al proceed at  $0 \text{ V}$  vs. the used aluminium reference electrode (AIRE), *i.e.* without overvoltage. The electrode process may formally be described by the following equations [15]



or



The  $\text{Br}^-$  ions formed are not sufficiently solvated and, consequently, not stable in aromatic hydrocarbon solution. The follow-up reaction proceeds



The overall electrode process is then described by the equation



The reversibility of the electrode process of  $\text{AlBr}_3$  reduction and aluminium oxidation was studied chronopotentiometrically, by logarithmic analysis of the ChP curves. In the cathodic branch of the curve no transition time is observed since the concentration of  $\text{AlBr}_3$  in the solution is high and thus, the limiting conditions are not reached. The anodic branch, representing the dissolution of cathodically deposited metal was treated according to the following equation [16]

$$E = E^\circ - \frac{RT}{zF} \ln \left( \frac{2j}{zF(\pi D)^{1/2}} \cdot \frac{s^{1/2}}{\text{mol dm}^{-3}} \right) - \frac{RT}{zF} \ln ((\tau^{1/2} - t^{1/2}) \cdot s^{-1/2}) \quad (I)^*$$

$j$  — current density,  $D$  — diffusion coefficient,  $\tau$  — transition time,  $t$  — time of reaching potential  $E$ ;  $E^\circ$ ,  $R$ ,  $T$ ,  $F$  have their usual meaning,  $z$  — charge number of the electrode process.

The results are presented in Fig. 2. Slope of the  $E - \log(\tau^{1/2} - t^{1/2}) \cdot s^{-1/2}$  line enables to calculate the charge number of the electrode process as it can be seen from eqn (I). The values thus obtained are summarized in Table 1. The results in the first line of Table 1 and curve 1 in Fig. 2 represent the spontaneous dissolution of aluminium with no current applied; this effect is dealt with in detail in Part II of this contribution. The values of  $z$  in Table 1 show that the charge number calculated approaches to the actual number of electrons transferred in the aluminium deposition/dissolution process, *i.e.*  $z = 3$ . The potential  $E_{\tau/4}$  which, according to the diagnostic criteria [16] should be independent of the current density, shifts positively with increasing anodic current density as can clearly be seen both from Fig. 2 and Table 1. All these phenomena lead to the conclusion that the electrode process of aluminium deposition/dissolution is not entirely reversible.

After addition of  $\text{PbBr}_2$  into the  $\text{AlBr}_3 + \text{KBr}$  solution in ETB, two equally high waves appear on the cathodic part of the CV record. The height of the waves increases with increasing  $\text{PbBr}_2$  concentration as it can be seen by comparing curves 2, 3, and 4 in Fig. 1. The plot of the cathodic CV limiting current *vs.*  $\text{PbBr}_2$  concentration shown in Fig. 3 is linear up to the  $\text{PbBr}_2$  concentration approx.  $5 \times 10^{-3} \text{ mol dm}^{-3}$ . Levelling off of the limiting current above this  $\text{PbBr}_2$

\* Note 1: The original equation derived by *Reinmuth* [16] in the form  $E = E_0 - \frac{RT}{zF} \ln \frac{2j}{zF(\pi D)^{1/2}} - \frac{RT}{zF} \ln (\tau^{1/2} - t^{1/2})$  has been changed for the above given form (I) upon the request of the Editor.

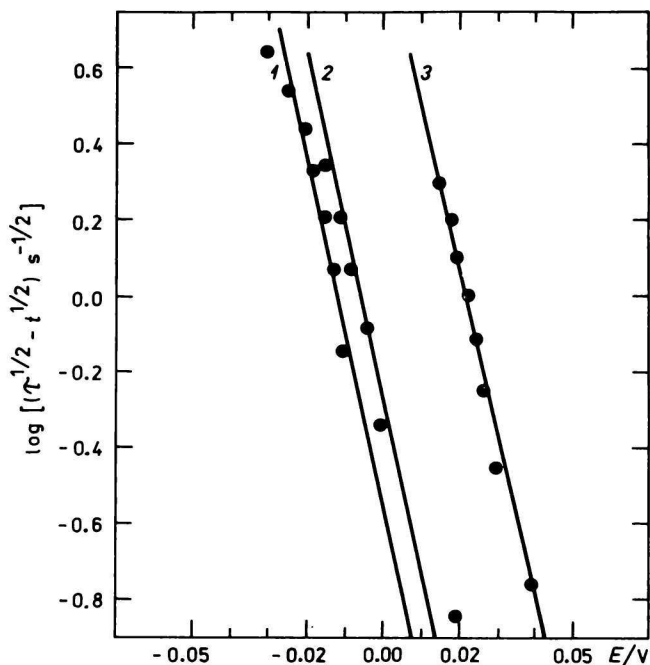


Fig. 2. Logarithmic analysis of the anodic branch of chronopotentiometric curves of aluminium deposition.  $c(\text{AlBr}_3) = 1.84 \text{ mol dm}^{-3}$ ;  $i$ : 1.  $0 \mu\text{A}$ ; 2.  $20 \mu\text{A}$ ; 3.  $40 \mu\text{A}$ .

Table 1

Logarithmic analysis of the chronopotentiometric record of anodic oxidation of aluminium in ETB electrolyte.

$c(\text{AlBr}_3)$ :  $1.86 \text{ mol dm}^{-3}$  (according to the relationship (1)).

$i \cdot 10^6/\text{A}$	$E_{\text{eq}}/\text{V}$	$\frac{\partial(E/\text{V})}{\partial \log((\tau^{1/2} - t^{1/2}) \cdot \text{s}^{-1/2})}$	$z$
		0	
20	-0.012	0.0215	2.74
40	+0.018	0.022	2.68
			$\bar{z} = 2.74$

concentration occurs. This effect may be explained as follows: dissolution of  $\text{PbBr}_2$  in the basic electrolyte proceeds most likely through formation of molecular or ionic aggregates with  $\text{Al}_2\text{Br}_6$  since in the solvent itself  $\text{PbBr}_2$  is insoluble. Similar associates formation was observed in case of other heavy metal bromides ( $\text{CuBr}$ ,  $\text{AgBr}$ ) in aromatic hydrocarbon solutions of  $\text{Al}_2\text{Br}_6$  [17]. Accord-

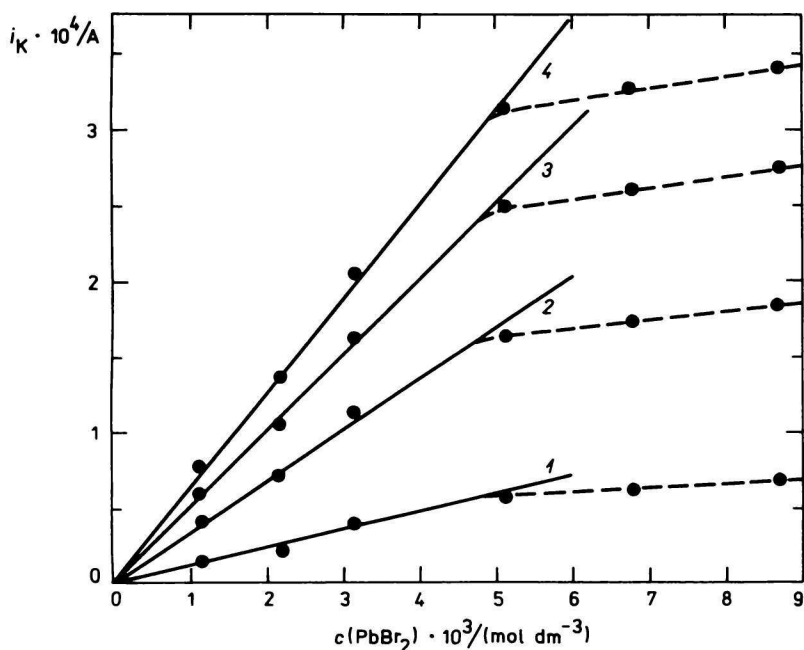


Fig. 3. The cathodic CV limiting current dependence on the  $\text{PbBr}_2$  concentration in ETB at various scan rates. Basic electrolyte:  $1.86 \text{ mol dm}^{-3} \text{ AlBr}_3$ ,  $0.8 \text{ mol dm}^{-3} \text{ KBr}$ . Scan rate: 1.  $0.0166 \text{ V s}^{-1}$ ; 2.  $0.0833 \text{ V s}^{-1}$ ; 3.  $0.166 \text{ V s}^{-1}$ ; 4.  $0.250 \text{ V s}^{-1}$ .

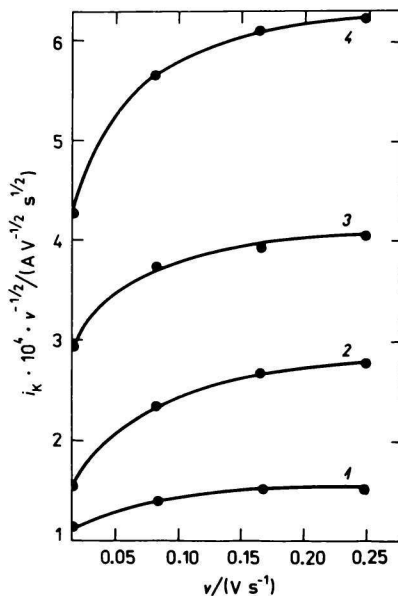
dingly, the formation of  $\text{PbBr}_2 \cdot \text{Al}_2\text{Br}_6$  or more likely  $\text{PbBr}^+ \cdot \text{Al}_2\text{Br}_7^-$  associate may be assumed owing to the high stability of  $\text{Al}_2\text{Br}_7^-$  anion. The limited dissolution of  $\text{PbBr}_2$  in the basic electrolyte may then be explained by a shortage of free neutral  $\text{Al}_2\text{Br}_6$  molecules available in the solution.

The addition of  $\text{PbBr}_2$  to the basic electrolyte results further in a negative shift of aluminium deposition potential of about 50–70 mV. The difference between deposition potentials of Al and Pb still is only 300 mV which is very profitable from the point of view of their simultaneous deposition from this electrolyte. Direct comparison of deposition potentials difference of both metals in organic and aqueous solutions is impossible since Al cannot be deposited from aqueous electrolyte. The difference of standard potentials of  $\text{Al}/\text{Al}^{3+}$  and  $\text{Pb}/\text{Pb}^{2+}$  redox pairs in aqueous solution, however, is 1400 mV. The low deposition potential difference for the two metals in the studied organic electrolyte may be ascribed mainly to the low solvation ability of the aromatic hydrocarbons in general, resulting in much weaker solvation of aluminium as compared with its hydration in water.

The effect of changing the sweep rate  $v$  is presented in Fig. 4 as well as by comparison of curves 4 and 5 in Fig. 1. Decrease in the sweep rate causes not

Fig. 4. The change of the CV cathodic current function  $i_k/v^{1/2}$  as a dependence on scan rate for various concentrations of  $\text{PbBr}_2$ . Other conditions as in Fig. 3.

$c(\text{PbBr}_2)$ : 1.  $1.12 \text{ mol dm}^{-3}$ ; 2.  $2.20 \text{ mol dm}^{-3}$ ; 3.  $3.13 \text{ mol dm}^{-3}$ ; 4.  $5.10 \text{ mol dm}^{-3}$ .



only decrease but also deformation of the cathodic CV current of the  $\text{PbBr}_2$  reduction. The diffusion control of the current is evident only for higher sweep rates as it is demonstrated by the dependence of current function  $i/v^{1/2}$  on  $v$  in Fig. 4: the plot approaches behaviour characteristic of diffusion-controlled current, *i.e.* independence on  $v$ , with increasing  $v$  values. Theoretical calculation of the diffusion coefficient from the linear independent part of the curves in Fig. 4 was carried out according to the following relationship valid for cathodic CV current in case of an insoluble product formation [18]

$$i_k = 3.67 \times 10^5 \cdot z^{3/2} \cdot D^{1/2} \cdot A \cdot v^{1/2} \cdot C \quad (2)^*$$

$A$  is the surface area of the electrode,  $v$  is sweep rate and  $C$  is the concentration of depolarizer, *i.e.*  $\text{PbBr}_2$  in the solution. The values of diffusion coefficient  $D$  obtained are  $(1.39 \pm 0.08) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  which is in good agreement with the literature value  $1.1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  [14].

The CV record in the range of low  $v$  values shows that a process causing decrease in the cathodic Pb deposition current is going on at low sweep rates being slow and thus having no chance to proceed at higher polarization change rates.

\* Note 2: The numerical constant includes universal constants  $R$  and  $F$  and 298 K for  $T$ .

Table 2

Logarithmic analysis of the chronopotentiometric record of cathodic reduction of  $\text{PbBr}_2$  in ETB electrolyte (according to the relationship (3))

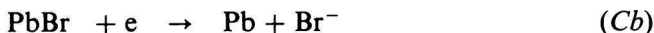
$c(\text{PbBr}_2)/(\text{mol dm}^{-3})$	$i \cdot 10^6/\text{A}$	$E_{\tau/4}/\text{V}^a$	$\frac{\partial(E/\text{V})}{\partial \log((\tau^{1/2} - t^{1/2}) \cdot \text{s}^{-1/2})}$	$\alpha z_a$	$\alpha$	$r^b$
$3.13 \times 10^{-3}$	60	0.228	0.0767	0.769	0.385	0.9926
	80	0.205	0.0953	0.619	0.309	0.9970
	100	0.188	0.0920	0.641	0.320	0.9960
					$\bar{\alpha} = 0.338$	
$5.1 \times 10^{-3}$	60	0.219	0.1280	0.461	0.230	0.9951

a) Values of  $E_{\tau/4}$  were calculated from the  $E - \log((\tau^{1/2} - t^{1/2}) \cdot \text{s}^{-1/2})$  plot.

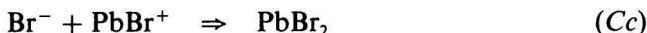
b)  $r$  is the correlation coefficient of the  $E - \log((\tau^{1/2} - t^{1/2}) \cdot \text{s}^{-1/2})$  line.



The suggested reduction process may then be described as follows



The released  $\text{Br}^-$  anion reacts immediately with a neutral molecule available, *i.e.* with  $\text{Al}_2\text{Br}_6$  according to (Bc) or as follows



In the reaction (Cc) original depolarizer  $\text{PbBr}^+$  is consumed and thus, the reduction current decrease follows. The possibility of the  $\text{PbBr}_2$  adsorption on the electrode resulting in blocking of a part of the active surface cannot be excluded.

The reversibility of  $\text{PbBr}_2$  electrode reduction process was studied again by logarithmic analysis of the cathodic branch of ChP curve, similarly as in the case of Al. The following equation was used for the evaluation [16]

$$E = E^\circ + \frac{RT}{\alpha z_a F} \ln \frac{2k_s^\circ s^{1/2}}{(\pi D_{\text{ox}})^{1/2}} + \frac{RT}{\alpha z_a F} \ln ((\tau^{1/2} - t^{1/2}) \cdot s^{-1/2}) \quad (3)^*$$

$\alpha$  is charge transfer coefficient,  $k_s^\circ$  is standard rate constant of the electrode process.

Data obtained by evaluation of the  $E - \log [(\tau^{1/2} - t^{1/2}) \cdot s^{-1/2}]$  plot are summarized in Table 2 and indicate the irreversibility of the process.

Anodic peaks appearing after addition of  $\text{PbBr}_2$  (Fig. 1) cannot be unambiguously ascribed to the oxidation of Pb and Al, respectively. The study of nature of these peaks will be presented in further parts of the contribution.

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\* Note 3: The original equation given by Reinmuth [16] in the form

$$E = E^\circ + \frac{RT}{\alpha z_a F} \ln \frac{2k_s^\circ}{(\pi D_{\text{ox}})^{1/2}} + \frac{RT}{\alpha z_a F} \ln (\tau^{1/2} - t^{1/2})$$

has been changed for the above given form (3) upon the request of the Editor.

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