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Electrodeposition of aluminium from a nonaqueous medium consisting of Al_2Br_6 and LiBr in ethylbenzene: the effects of additives

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A search was conducted to find suitable additives to act as levelling agents in the electrodeposition of aluminium from a nonaqueous bath consisting of Al_2Br_6 and MBr in an aromatic hydrocarbon. Two nitro-compounds were found to act effectively. The current–potential relationships were determined in the presence of different concentrations of these compounds in stirred and unstirred solutions and the effects observed were interpreted on the basis of a simple model. The increase of overpotential (at constant current density) with increasing mass transport rate was used as a qualitative criterion for the identification of an effective leveller.

1. Introduction

Aluminium cannot be electrodeposited from aqueous solutions or from any other protic solvent due to the rapid decomposition of the solvent which occurs before the potential for discharge of the metal is reached. Numerous attempts have been made in the past to find a suitable solvent system which could be used as an industrial plating bath. These results have been reviewed in several publications [1–4].

One of the most suitable systems found for this purpose consists of a solution of Al_2Br_6 and an alkali bromide in an aromatic hydrocarbon. Apart from its practical importance as a possible plating bath for aluminium, this system exhibits unusual electrochemical properties. Its dielectric constant is low while its specific conductivity is relatively high (up to 6 $m\Omega^{-1}\,cm^{-1}$ at room temperature).

The study of this and related systems was started by Plotnikov and his co-workers in 1928 [5]. A recent review was presented by Gileadi and co-workers [6] in 1977. The industrial need for a high-quality aluminium coating and the desire to find an alternative for cadmium, due to its toxicity, caused renewed interest in the development of an aluminium plating bath [4, 7–11]. Some of the chemical and electrochemical properties of this sytem have been studied in our laboratory [6, 12–20] and a summary was presented very recently [21]. Good aluminium electrodeposits can be obtained from this type of bath on copper, steel and other conducting surfaces, as discussed earlier [4, 11]. The Faradaic efficiency is close to 100% both at the anode and at the cathode, and the bath is stable for periods of many months if properly maintained.

The purpose of the present work is to evaluate the properties of a number of additives which could be used in this bath to improve the quality of plating, mainly by decreasing grain size and enhancing levelling. The increase of overpotential with increased stirring was taken as a criterion for the activity of a given compound as a levelling agent [22–26]. Of a large number of materials scanned in this manner only two nitro-compounds were found sufficiently active to warrant further study.

2. Experimental

2.1. *Solutions*

All experiments were performed in rigorously dried solutions of Al_2Br_6 and LiBr in ethyl benzene. The methods of preparation of the solutions and the purification and drying of the compounds have been described elsewhere [6, 12, 18].

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The addition agents studied in detail were purified by vacuum distillation over a molecular sieve. Stock solutions containing known amounts of the addition agent in ethylbenzene were prepared and used to make up the required concentration of the addition agent in the test solution. All experiments were performed in a glove box (VAC, model DL001-D-G) filled with highly purified argon which was continuously circulated through a catalytic purifier (VAC, model HE-493 DRI-TRAIN).

2.2. *Cells and electrodes*

The preliminary survey of possible addition agents was performed in a three-electrode cell in which cylindrical symmetry was maintained [12]. A gold wire, freshly coated *in situ* with aluminium served as the working electrode and pure aluminium wires (Hopkin and Williams, 99.99% purity) served both as the counter and reference electrodes. The solution was stirred with a magnetic stirrer in these preliminary experiments.

Most of the results presented below were measured in a two-compartment cell [20]. A rotating-disc gold electrode, freshly coated *in situ* with aluminium served as the working electrode. An aluminium wire located in a separate compartment and connected to the main compartment by a Luggin capillary was employed as the reference electrode. A circular aluminium sheet (Goodfellow Metals, 99.99% purity), placed parallel to the working electrode at a distance of about 1 cm, served as the counter electrode. All electrodes were prepared and cleaned as described earlier [18]. The cell was closed with tapered glass joints and Teflon plugs and was kept inside the glove box during the experiments.

2.3. *Electrical measurements*

A preliminary survey of candidate materials to be used as additives was performed galvanostatically, employing an Elron model CHG-1 galvanostat. The overpotential was recorded on an HP, model 7030 AM strip chart recorder with a home-made impedance matching unit (input impedance $10^9\,\Omega$). The potential drop due to solution resistance was corrected for as described earlier [12].

The results presented below were obtained with a rotating-disc system (Pine Instruments, model ASR-2) which was placed inside the glove box, while the r.p.m. control unit was located outside. Simultaneous measurement of ohmic drop in the solution and of overpotential was performed with a unit specially designed for this purpose [27]. Both quantities were recorded on a dual-pen strip chart recorder (Telrad, model 712, input impedance $5 \times 10^8\,\Omega$). All potentials were measured versus a reversible aluminium electrode (RAlE) in the same solution.

3. Results

3.1. *Survey of addition agents*

When no additive is present and the electrodeposition reaction is at least partially controlled by mass transport (as observed in the present system [20]), increasing the stirring rate should decrease the overpotential. In the presence of an additive which acts as an effective levelling agent, increasing the stirring rate *increases* the overpotential, since the molecules of the additive absorbed on the surface inhibit the electrodeposition of the metal and the rate at which they reach the surface is increased.

Sixteen different compounds were tested, among them tetra-alkylammonium salts, pyridinium derivatives, phosphonium salts, DMF, DMSO and propylene carbonate. A family of nitrocompounds was found to be active as levelling agents. The behaviour of two members of this family, nitromethane (N1) and 2-nitropropane (N3), is shown in Figs. 1 and 2. In each experiment the current was held constant and the potential recorded without stirring. The magnetic stirrer was then turned on and the change in potential ΔV was recorded. This is plotted as a function of current density for different concentrations C_1 of the additives. In the absence of additives the overpotential is found to decrease with stirring ($\Delta V < 0$) as expected, and the absolute value of ΔV increases with increasing current density due to a higher degree of depletion of the diffusion layer in the unstirred solution. In the presence of the levelling agent the overpotential increases when stirring is started at low current densities. Since ΔV increases due to the presence of the additive and decreases (i.e. becomes less

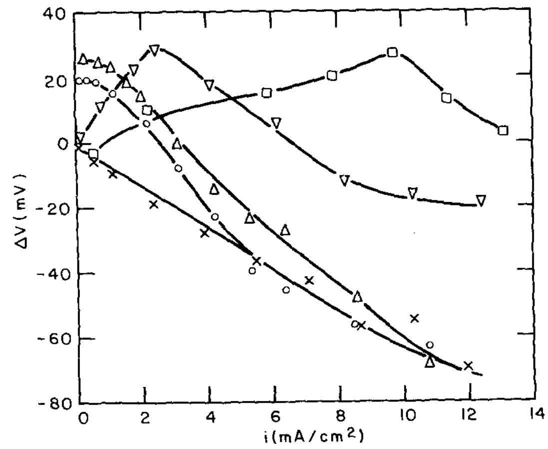

Fig. 1. The change in potential caused by stirring as a function of current density for different concentrations of additive N1. Al_2Br_6, 1.0 M; LiBr, 1.0 M; x, without additive; ○, 0.3 mM; △, 0.5 mM; ▽, 1.0 mM; □. 1.5 mM.

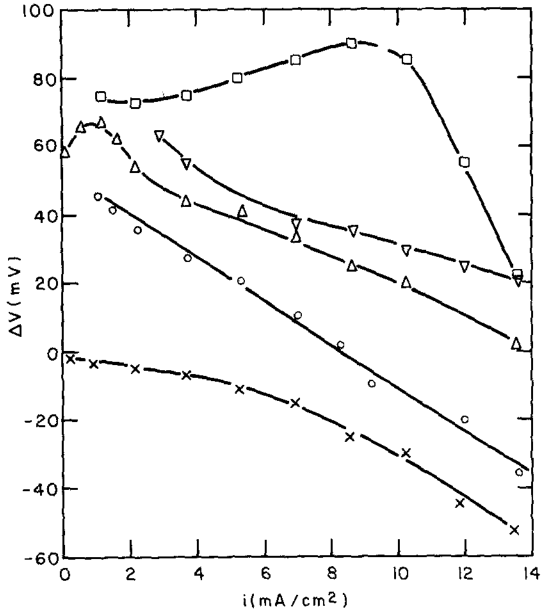

Fig. 2. Same as Fig. 1 but for the additive N3. Al_2Br_6, 1.0 M; LiBr, 0.68 M; x, without additive; ○, 0.5 mM; △, 1.0 mM; ▽, 2 mM; □, 4 mM.

positive or more negative) with increasing current density, the variation of ΔV with i and C_1 is complex. At low values of C_1, the measured ΔV is positive at low current density and reaches negative values at higher current densities. At higher concentrations of the additive, ΔV first rises with i, goes through a maximum and declines at high current densities†, as seen in Figs. 1 and 2.

When the current is applied to an aluminium working electrode freshly deposited in the presence of either N1 or N3, a potential peak is observed. The peak height is up to 70 mV in the presence of N1 and up to 200 mV in the presence of N3 and its duration is between a few milliseconds and several minutes, indicating that the freshly plated surface becomes almost entirely covered by one or more layers of adsorbed molecules of the additive or its reduction products, which are subsequently buried under new layers of electrodeposited aluminium.

The effect of a low concentration (0.1 mM) of additive N3 on the grain size of electroplated aluminium is shown in the photomicrographs in Fig. 3. The average grain size is found to decrease by about a factor of four.

The two levelling agents N1 and N3 were found to be unstable in solution. Their activity, measured as the increase of overpotential with stirring (cf. Figs. 1 and 2), declines gradually with time over a period of several hours.

3.2. *Measurements with the rotating-disc electrode (RDE)*

Steady-state current–overpotential plots obtained in the presence of additive N3 on a rotating-disc electrode are shown in Figs. 4 and 5. The overpotential is seen to increase both with concentration of the additive and with rotation rate, indicating (a) that the additive had an inhibiting effect on the electrodeposition reaction and (b) that it was consumed at the electrode and that its effect was enhanced by increasing the rate of mass transport to the electrode surface. It should be noted that the concentration of additive used in these experiments was about an order of magnitude lower than those employed when a stationary electrode was used (Figs. 1 and 2) due to the higher efficiency of stirring at the RDE.

A region of negative reaction resistance, where the overpotential decreases with increasing current density, was observed in all these experiments. The current density $i_{\min}$ at the minimum of the η–i

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† In the presence of 4.0 mM of additive N3, oscillations of the potential were observed. The corresponding values of ΔV given in Fig. 2 are averages.

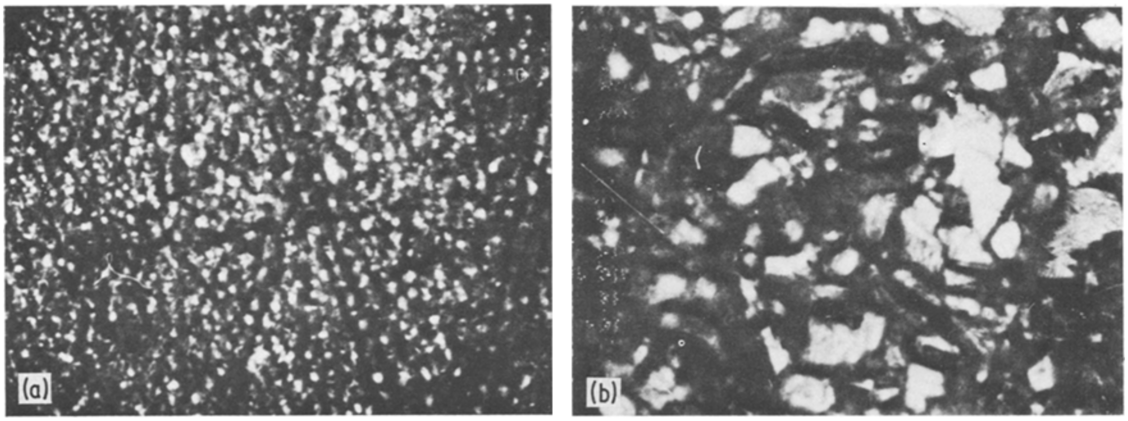

Fig. 3. Photomicrographic comparison of the grain size of aluminium electrodeposited (a) in the presence of additive and (b) in its absence.

plots in Figs. 4 and 5 is seen to depend both on the concentration of the additive and on the rotation rate. The same results were obtained when measurements were taken at successively increasing or decreasing current densities.

Overpotential transients caused by a sudden change in rotation rate or current density are shown schematically in Figs. 6 and 7 respectively. It is important to note that all the phenomena described above were specific to the cathodic electrodeposition process. The additive had no effect whatsoever on the rate of anodic dissolution of aluminium in the same solution.

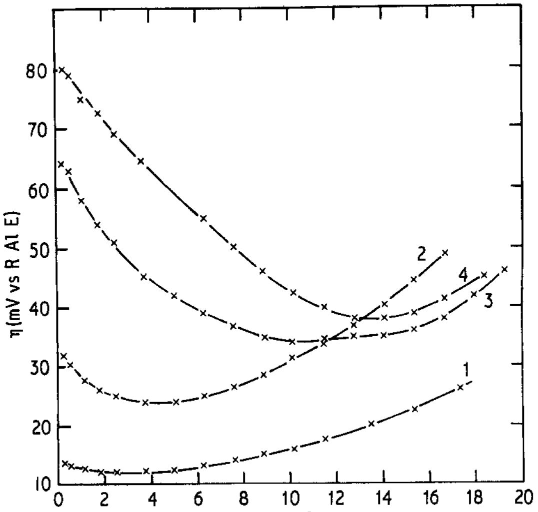

Fig. 4. The effect of concentration of N3 on the cathodic polarization curve at a rotation rate of 100 r.p.m. Al_2Br_6 1.0 M; LiBr, 0.80 M; 1, 0.05 mM; 2, 0.08 mM; 3, 0.15 mM; 4, 0.20 mM.

4. Discussion

4.1. *The levelling effect*

The effects of the levelling agents N1 and N3 observed above will be discussed in terms of a competition between two parallel reactions, namely, the electrodeposition of aluminium and the formation of a partial layer of molecules of the additive, which inhibits the former reaction. The molecules of the additive or its reduction product are consumed at the electrode surface by being incorporated into the metal deposit and buried under subsequent layers of the metal. It should also be borne in mind that the concentration of the levelling agents is about three orders of magnitude lower than that of the electroactive species for aluminium deposition. Thus the rate of adsorption and/or reaction of the additive at the surface is totally controlled by mass transport even at the lowest current density applied, while the rate of aluminium deposition is partially mass-transport controlled, to an extent depending on the current density applied.

The additive has no effect on the overpotential at the anode, either because it is not adsorbed at the potential prevailing at the anode or because adsorbed molecules can block the surface and slow down electrodeposition of the metal. They do not, however, effect the rate of its anodic dissolution, since they are continuously removed with the layers of dissolving aluminium.

The data shown in Figs. 1 and 2 can be readily interpreted in terms of the above assumptions. In

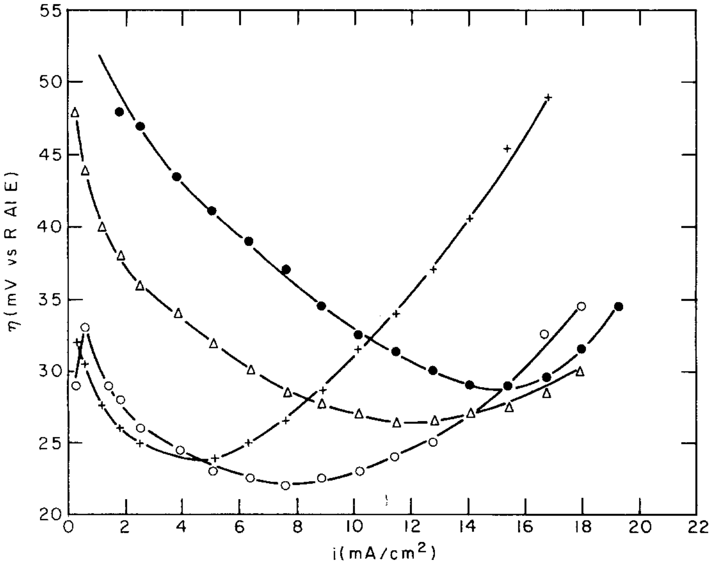

Fig. 5. The effect of rotation rate on the cathodic polarization curve in the presence of 0.08 mM additive N3. Al$_2$Br$_6$, 1.0 M; LiBr, 0.80 M; +, 100 r.p.m. ○, 225 r.p.m.; △; 400 r.p.m.; ●, 900 r.p.m.

the absence of additives, the diffusion layer in unstirred solution is partially depleted. Starting the stirring then causes a decrease in overpotential ($\Delta V < 0$). At low concentrations of additive and low current densities the overpotential increases when stirring is started ($\Delta V > 0$) because the larger supply of the additive to the surface enhances inhibition, while the diffusion layer is not significantly depleted of the electroactive species for metal deposition. As the current density is increased the change of overpotential due to a higher rate of supply of the additive remains essentially constant, while the decrease of overpotential due to a higher rate of supply of the aluminium-containing species increases, until the net effect is a decrease of overpotential with increased stirring ($\Delta V < 0$). At higher concentrations of the additive the two opposing effects lead to a maximum in the plot of ΔV versus i. The region of the maximum can be identified as the region of most effective levelling action [23, 28, 29].

The transient phenomena shown schematically in Figs. 6 and 7 can be understood in terms of the same model (cf. also [30, 31]). Curve a in Fig. 6 corresponds to a high current density and relatively low concentration of additive, yielding a decrease of overpotential with increased stirring ($\Delta V < 0$). As the rotation rate is increased suddenly the overpotential drops sharply due to the increased supply of electroactive species to the surface. Subsequently, more of the levelling agent reaches the surface, increasing the overpotential until a new steady state is reached. Curve b is taken at a lower current density. At the moment the rotation rate is increased the overpotential drops due to the increased supply of the electro-

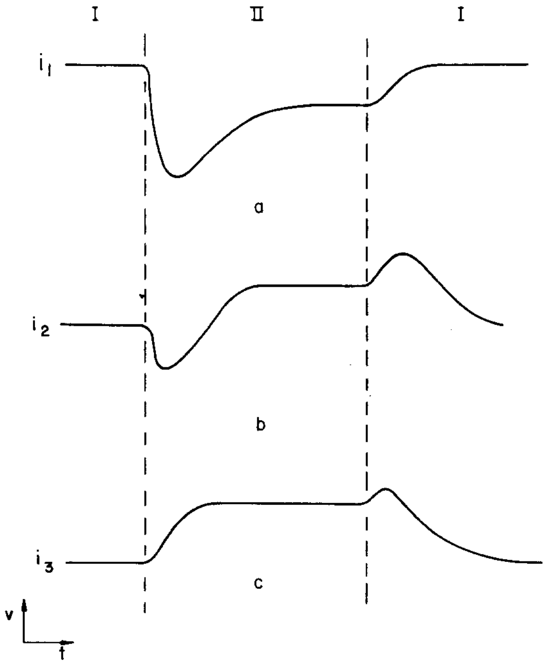

Fig. 6. Schematic potential–time transients caused by changing the rotation rate ω at constant current density in the presence of N1 or N3. $\omega_I < \omega_{II}$; $i_1 > i_2 > i_3$.

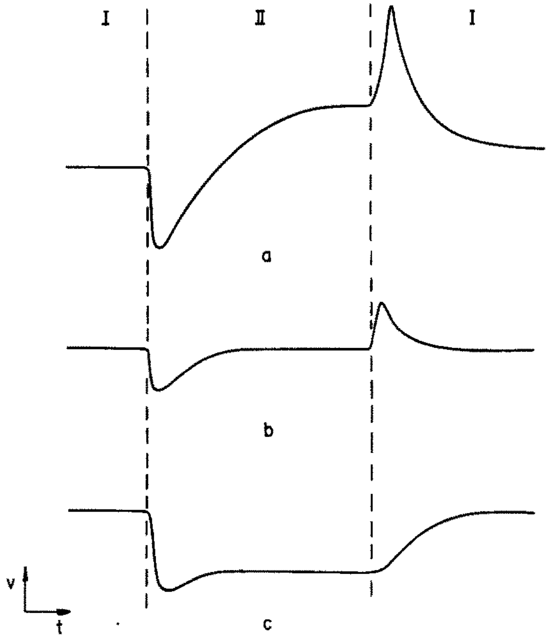

Fig. 7. Schematic potential–time transients with changing current density at constant rotation rate in the presence of N1 or N3. $i_{I} > i_{II}$; a, region of negative reaction resistance ($i < i_{min}$); b, at $i = i_{min}$; c, high current density region ($i > i_{min}$).

active species, but the new steady state is reached at a higher overpotential ($\Delta V > 0$) since the enhanced inhibition outweighs the effect of increased mass transport. In Fig. 6c the current density is quite low so that the diffusion layer is not significantly depleted even at the lower rotation rate. Increasing the rate of rotation therefore causes only an increase of overpotential due to a high rate of supply of the levelling agent to the electrode surface.

In Fig. 7 the effect of changing the current density at constant rotation rate is depicted. Curve a was taken in the region of low current density, corresponding to a negative reaction resistance (cf. Figs. 4 and 5). As the current density is decreased, the overpotential drops momentarily, as would be expected for any electrode reaction. Subsequently it grows, to a higher value, due to the increased relative rate of supply of the levelling agent to the surface, leading to an increase in θ_1. Much the same is observed in curve b, taken at the minimum in an η–i curve, such as shown in Figs. 4 and 5. In this region of the minimum, changing the current density has very little effect on the steady-state overpotential, as observed. At still higher current densities (curve c) decreasing i decreases the overpotential to a lower steady-state value, with only a little dip during the transient.

4.2. *The minimum in the polarization curve*

The minima in the η–i curves shown in Figs. 4 and 5 are the result of two opposing changes taking place simultaneously, namely, changes in the rate of formation of new layers of electrodeposited aluminium and in the rate of blocking of the surface by molecules of the levelling agent. At low current densities increasing the current increases the rate of formation of new surface while the rate of blocking of the surface is constant (due to the low concentration of the additive, its limiting current is already reached when the overall observed current density is low). The activation overpotential for aluminium deposition is rather low [12, 14] and the concentration polarization is negligible in this region, leading to an overall net decrease of η with increasing i. Beyond a certain current density i_{min} the effect of decreasing overpotential due to the increased rate of formation of the new surface is outweighed by the increased concentration overpotential and a net increase of η with increasing i is observed. Increasing the rate of rotation increases the rate of supply of the levelling agent to the surface. This is expected to shift the minimum in the polarization curves to higher values of the current density, as observed experimentally. A similar behaviour was reported by Johnson and Turner [32].

4.3. *Quantitative treatment*

Based on the experimental observations presented above and the qualitative description of these phenomena, a model is proposed which can correlate the experimental parameters quantitatively. Assume, for simplicity, that the overpotential is low so that the i–η relationship is linear. We then have

$$i = \frac{\eta_a}{R}(1 - \theta_1) \tag{1}$$

where i is the total current density observed, η_a is the activation overpotential, R is the reaction resistance and θ_1 is the fractional surface coverage by molecules of the additive which acts as the levelling agent. Multiplying by the factor of $(1-\theta_l)$ is the simplest way of taking into account the effect of an additive or impurity which blocks the surface. It neglects the effects which an adsorbed species can have on the structure of the double layer and in particular the 'induced heterogeneity' which it can cause [33, 34] but is nevertheless often used when there is a lack of detailed information. In our previous studies [12, 20] the reaction resistance was estimated at $R \leqslant 0.2\,\Omega\,\mathrm{cm}^2$ for a clean aluminium surface. It was also shown [20] that at a rotation rate of 100 r.p.m. and current densities below approximately $20\,\mathrm{mA\,cm^{-2}}$ the reaction rate was mainly mass-transport controlled and obeyed the simple relationship:

$$\eta_c = Ki/\omega^{1/2} \tag{2}$$

where η_c is the concentration overpotential and K is an appropriate constant which depends on the concentrations of Al_2Br_6 and KBr. The linear η–i relationship observed according to Equation 2 indicates that the applied current densities were small compared to the mass-transport-limited current density i_L.

The activation overpotential η_a depends, at constant current density, both on the concentration of the electroactive species at the surface and on the coverage θ_l by the levelling agent which blocks the surface. Since $i/i_L \ll 1$ in the present measurements, the effect of mass transport on η_a will be neglected[†]. The total measured overpotential can then be written simply as

$$\eta = \eta_a + \eta_c = \frac{iR}{1-\theta_l} + \frac{iK}{\omega^{1/2}}. \tag{3}$$

The blocking of the surface is a result of reduction of additive molecules reaching the surface by diffusion. This mass-transport-controlled rate can be expressed by

$$V_T = k_T i_l \tag{4}$$

where i_l is the partial current density for reduction and adsorption of the additive and k_T is a constant. The additive (or its reduction product) is consumed mainly by being incorporated into the metal deposit. The rate of incorporation V_{inc} can be expressed by:

$$V_{inc} = k_{inc}\theta i_{Al} \tag{5}$$

where i_{Al}, the partial current density for electrodeposition of Al, is practically equal to the total current density i. At steady state the rate V_T at which additive molecules reach the surface is equal to the rate of incorporation (cf. Equation 26 in [23]), hence

$$\theta_l = ki_l/i. \tag{6}$$

Due to the low concentration of the additive its partial current is mass-transport limited over the whole range of current densities employed for electrodeposition of the metal, hence

$$i_l = k_l C_l \omega^{1/2} \tag{7}$$

where k_l is a constant derived from the Levich equation for an RDE. The high values of the overpotential observed at low current densities (Figs. 4 and 5) and the very high transient overpotential (up to 200 mV) on application of a cathodic current to an aluminium working electrode previously immersed in a solution containing additive, lead to the conclusion that the additive reacts with aluminium on open circuit and that θ_l is close to unity. The fact that $\theta_l \simeq 1.0$ while $i_{Al} > 100\, i_l$ shows that the incorporation of the adsorbed species into the deposit is a very inefficient process. Assuming the validity of the adatom deposition mechanism for this case, it can be concluded that during plating the progressive steps push the adsorbed molecules of the additive (or its reduction product) from the lower metallic step to the upper, newly formed step. In this way no new clean metallic surface is formed and θ_l remains always close to unity.

Combining Equations 3, 6 and 7 leads to:

$$\eta = \frac{iR}{(1-PC_l\omega^{1/2})/i} + \frac{iK}{\omega^{1/2}} \tag{8}$$

where P is a constant.

Equation 8 describes the curves exhibited in Figs. 4 and 5. At low current densities, decreasing i decreases the denominator much faster than the numerator, resulting in the increase of the overpotential. At high current densities, $PC_l\omega^{1/2}/i$ may be neglected, and one obtains the same equation as derived in the absence of an additive. On differentiating Equation 8 with respect to i, i_{min} is obtained:

[†] This approximation is even more valid in the vicinity of i_{min}, which is most relevant for the verification of the model proposed here.

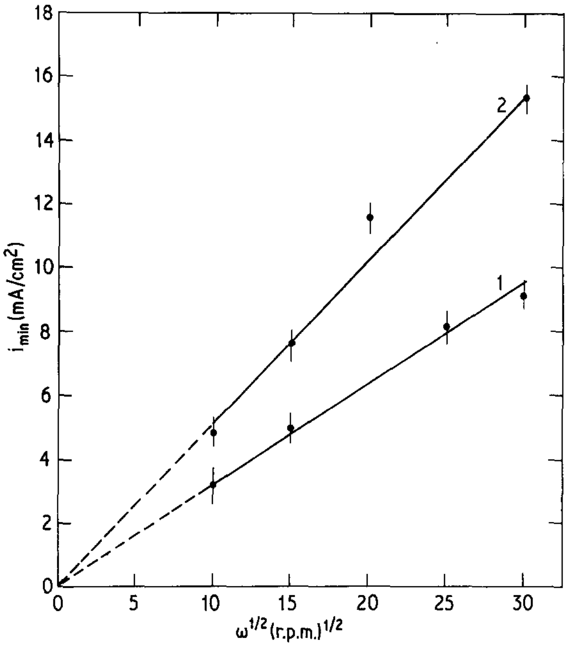

Fig. 8. Plots of $i_{\min}$ versus $\omega^{1/2}$ at two concentrations of N3. Al_2Br_6, 1.0 M; LiBr, 0.80 mM. 1, 0.05 mM; 2, 0.08 M.

$$i_{\min} = PC_1\omega^{1/2}\left[1+\left(1-\frac{K}{R\omega^{1/2}+K}\right)^{1/2}\right]. \qquad (9)$$

Since it was found experimentally [20] that $K > R\omega^{1/2}$, Equation [9] can be written approximately as:

$$i_{\min} \simeq PC_1\omega^{1/2}. \qquad (10)$$

Equation 10 predicts a linear dependence of $i_{\min}$ on the square root of rotation rate and on additive concentration. Figs. 8 and 9, as drawn from Figs. 4 and 5 and other results, show excellent agreement with this prediction. These findings support the model proposed above for the effect of the additives on the η–i relationship.

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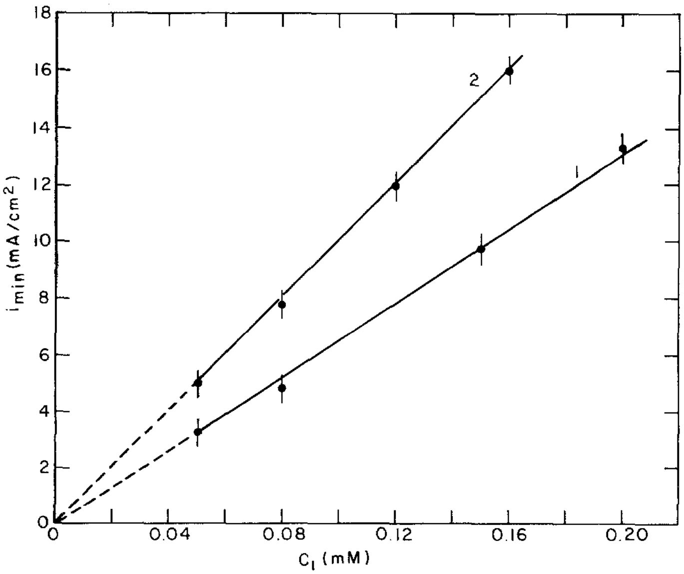

Fig. 9. Plots of $i_{\min}$ versus the concentration of additive N3 at two rotation rates. Al_2Br_6, 1.0 M; LiBr, 0.80 M; 1, 100 r.p.m.; 2, 225 r.p.m.

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