Influence of tartaric acid on the electrodeposition of silver from aqueous $AgNO_3$ solutions

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Silver electrodeposition from aqueous $AgNO_3$ solutions never gives compact, smooth plates unless an organic additive such as tartaric acid (H_2A) is used as growth inhibitor. However, depending on the bulk pH, H_2A may exist either as a neutral molecule of H_2A or as dissociated entities such as HA^- or A^{2-}. We have shown previously that the relevant parameter governing growth inhibition was the activity, α_{HA^-}, of tartaric monoanions when silver was plated from a solution of constant $AgNO_3$ concentration. The aim of the present work is to show what happens when this concentration is no longer constant. In these conditions, the relevant parameter governing growth inhibition is proved here to be the bulk concentration of a neutral complex Ag(HA) formed in the solution between Ag^+ and tartaric monoanions HA^-. On this concentration depend most of the structural features of Ag deposits, e.g. their grain size, superficial roughness and even the amount of incorporated organic material.

1. Introduction

Silver electrodeposits prepared from $AgNO_3$ solutions are known to consist of independent crystals which, under given plating conditions, may degenerate as dendrites [1–8]. A lot of additives, mainly organic, have therefore been tried in order to prevent any dendritic growth and favour the formation of smooth, coherent silver plates. Tartaric acid (H_2A), whose effect was discovered very early [9], has proved to be among the most effective growth inhibitors [5–11]. But, in so far as potassium sodium tartrate (NaKA) shows the same inhibiting effect as H_2A [4] and leads to the same tartaric entities after dissociation and recombination with H^+, it must be concluded that the effect arises in both cases from either the molecular form of tartaric acid H_2A, or from a dissociated form like HA^- or A^{2-}.

We have shown in previous work that a discrimination can be made between the three forms [12] and we thus found that for Ag plated from a 0.5M $AgNO_3$ solution, the relevant parameter hindering dendritic growth was the concentration of monovalent anions HA^-, whatever the concentrations of every other ionic and non-ionic entities in the solution [8]. From that conclusion we assumed that a neutral complex such as [Ag(HA)] could be implicated in the inhibition process; it was then necessary to explore various $AgNO_3$ concentrations to check this assumption. And the best way seemed to decrease [$AgNO_3$] since dendritic growth is favoured in dilute solutions [1, 2, 3, 7].

2. Experimental conditions

Four concentrations of $AgNO_3$ (Merck p.a.) are studied here ranging from 0.2 to 0.05 M. The total concentration, C_{H_2A}, of tartaric acid (L(+) Carlo Erba RP-ACS) is 0.015M in every case; a simple way to obtain from that constant value different HA^- concentrations is to vary the solution pH by progressive additions of a 1M HNO_3

Table 1. Composition of AgNO$_3$–tartaric acid (H$_2$A) solutions which give coherent Ag electrodeposits, $C_{H_2A} = 0.015$ *M*

(a) [AgNo$_3$] = 0.2 M				(b) [AgNO$_3$] = 0.1 M			
Run	[HNO$_3$]	pH	$\alpha_{HA^-} \times 10^5$	Run	[HNO$_3$]	pH	$\alpha_{HA^-} \times 10^5$
A1	0.02	1.802	83.0	B1	0.005	2.194	189.2
A2	0.03	1.611	54.6	B2	0.010	2.049	140.6
A3	0.05	1.411	34.9	B3	0.020	1.784	79.8
A4	0.07	1.283	26.1	B4	0.040	1.523	44.8
A5	0.10	1.164	19.9	B5	0.060	1.366	31.5
A6	0.20	0.935	11.8	B6	0.080	1.252	24.4
A7	0.40	0.710	7.0	B7	0.100	1.142	19.0
A8	0.60	0.501	4.4	B8	0.200	0.936	11.9
				B9	0.400	0.684	6.7
				B10	0.600	0.530	4.7

(c) [AgNO$_3$] = 0.075 M				(d) [AgNO$_3$] = 0.05 M			
Run	[HNO$_3$]	pH	$\alpha_{HA^-} \times 10^5$	Run	[HNO$_3$]	pH	$\alpha_{HA^-} \times 10^5$
C1	0.005	2.182	184.7	D1	0.005	2.200	191.5
C2	0.010	1.996	125.8	D2	0.010	2.019	132.0
C3	0.020	1.778	78.8	D3	0.020	1.778	78.8
C4	0.030	1.630	56.9	D4	0.030	1.621	55.8
C5	0.040	1.510	43.6	D5	0.040	1.520	44.5
C6	0.050	1.424	35.9	D6	0.050	1.413	35.0
C7	0.100	1.165	20.0	D7	0.100	1.168	20.1
C8	0.200	0.937	11.9	D8	0.200	1.000	13.7
C9	0.300	0.778	8.3	D9	0.400	0.700	6.9
C10	0.400	0.700	6.9	D10	0.600	0.545	4.8
C11	0.600	0.578	5.2				

solution (Merck Titrisol). The electrolytic solution is renewed after each experiment to avoid any modification of C_{H_2A} due to a cathodic consumption of tartaric acid. The electrolytic double cell, with a capacity of 300 ml, is maintained at $25.00 \pm 0.02°$ C by means of a water flow thermostat (Haake KG Ultrathermostat NBS).

Reproducibility of hydrodynamic conditions is ensured by use of a rotating disc electrode ($\phi = 17.3$ mm) with constant angular speed (1000 rev min^{-1}). Cathode and anode are both made of high purity silver (99.999% Matthey Chemicals). The anode is a broad flat disc ($\phi = 60$ mm) kept at a constant distance (25 mm) in front of the rotating cathode. All electrical insulations are made with Teflon.

Prior to deposition the cathodic surface is mechanically polished with emery papers of decreasing roughness (down to 800 mesh) under a strong water flow. Then a chemical polishing is performed with a mixture of CrO$_3$ and HCl [13, 14]. The current is galvanostatically controlled so as to give a constant current density

of 2A dm^{-2} over 47 min, which leads to deposits of constant thickness ($\simeq 60$ μm).

An exact measurement of the charge passing through the cell is obtained by means of a charge integrator (Tacussel IG 5 LN). This allows accurate determination of the theoretical weight, p, of the deposits. From the experimental values, which are systematically greater than p, we calculate the weight increase Δp and the ratio $\Delta p/p$.

The surface morphology is examined by means of a scanning electron microscope (Cambridge S 600) and the roughness determined with a Perthen FTK 7 profilograph.

3. Results and discussion

3.1. *Effect of monoanions activity,* α_{HA^-}

Four series of Ag plates have been studied here, each series corresponding to a definite AgNO$_3$ concentration. Table 1 gives the main composition parameters for every case. Since the four different solutions do not have the same ionic strength, I, we have to determine the different activities
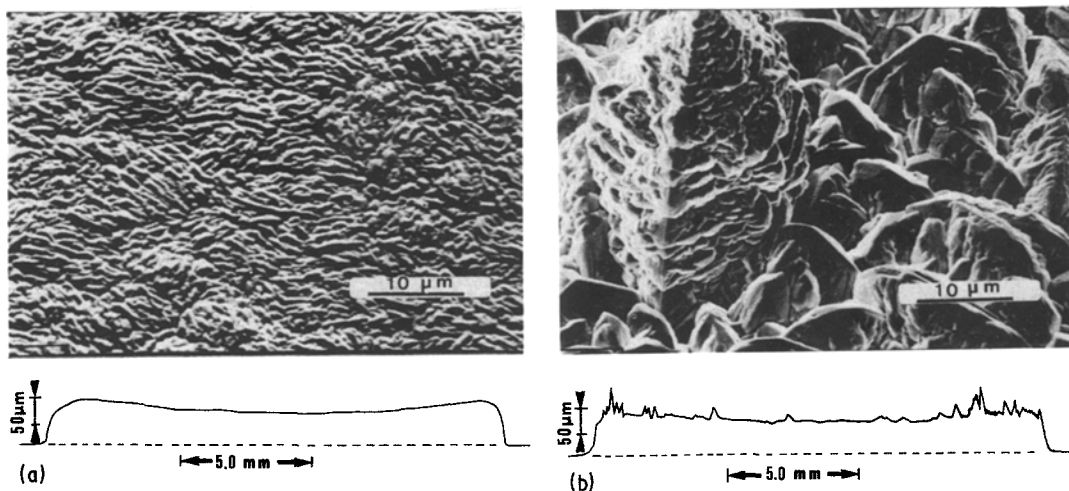
Fig. 1. Influence of monoanion activity on surface morphology (SEM micrographs) and roughness (curves) of two deposits prepared from an 0.1M AgNO$_3$ solution. (a) Deposit B2 ($\alpha_{HA^-} = 140.6 \times 10^{-5}$ M), (b) deposit B9 ($\alpha_{HA^-} = 6.7 \times 10^{-5}$ M).

α_{HA^-}. We must first of all know the dissociation constants K_1 and K_2 of tartaric acid. Values taken from literature [15–18] are obtained under conditions quite different from ours; it was therefore necessary to redetermine both constants. For this purpose the application of Speakman's method to potentiometric titration curves [19, 20] gave, respectively, $K_1 = (9.2 \pm 0.1) \times 10^{-4}$, i.e. p$K_1 = 3.03$, and $K_2 = (4.6 \pm 0.1) \times 10^{-5}$, i.e p$K_2 = 4.34$.

All deposits in a given series are obtained with the same AgNO$_3$ concentration, hence they must exhibit the same dependency between α_{HA^-} and surface morphology as was depicted in our earlier paper [8], i.e. the greater is α_{HA^-} the smoother is the corresponding deposit. Fig. 1 illustrates such a tendency for two deposits of series B. Both come from a 0.1M AgNO$_3$ solution but B2 corresponds to an α_{HA^-} value 20 times greater than in the B9 case. That B2 is far smoother than B9 confirms that α_{HA^-} is a relevant parameter for growth inhibition.

3.2. Effect of AgNO$_3$ concentration

To answer the question of whether α_{HA^-} is the unique factor governing inhibition we must keep it constant and vary other parameters. In Fig. 2 two deposits (A7 and C10) prepared from solutions with nearly the same activity α_{HA^-} but

different AgNO$_3$ concentrations, 0.2M and 0.075M, respectively, are compared.

It is obvious From Fig. 2 that growth inhibition depends equally on AgNO$_3$ concentration; more dilute solutions give less coherent deposits. Of course this result was not unexpected since dilution favours dendritic growth. But it is noteworthy that the same conclusion holds even in the presence of an efficient growth inhibitor such as tartaric acid.

3.3. Characterization of growth inhibition

Fuseya and Murata [6] were the first to detect an incorporation of organic molecules into silver deposits obtained with tartaric acid. We have shown in our previous work that the ratio $\Delta p/p$ is closely related to structural parameters such
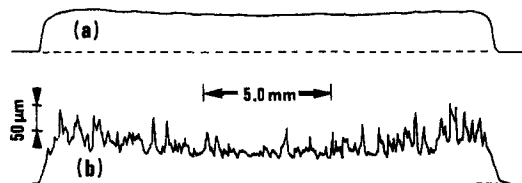

Fig. 2. Influence of AgNO$_3$ concentration on surface roughness of two deposits prepared from solution with same activity $\alpha_{HA^-} = 7 \times 10^{-5}$ M. (a) Deposit A7 ([AgNO$_3$] = 0.2M), (b) Deposit C10 ([AgNO$_3$] = 0.075 M).
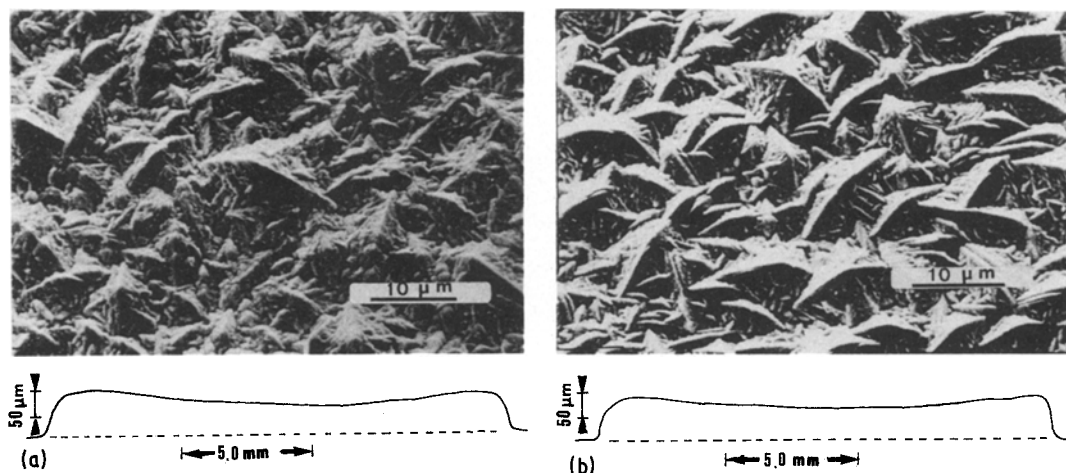
Fig. 3. Surface morphology (SEM micrographs) and roughness (curves) of two deposits obtained from quite different solutions but exhibiting the same $\Delta p/p$ value of 2.6%. (a) Deposit A6 ($AgNO_3$ 0.2 M; $\alpha_{AH} = 11.8 \times 10^{-5}$ M), (b) deposit B7 ($AgNO_3$ 0.1 M; $\alpha_{HA^-} = 19.0 \times 10^{-5}$ M).

as surface roughness and morphology; more incorporations means smoother deposits with finer grain size [8]. Then it should be possible to characterize 'growth inhibition' by a quantitative parameter such as $\Delta p/p$ provided that the equivalence between both parameters is preserved in the present working conditions.

A measurement of $\Delta p/p$ for both deposits of Fig. 2 gives 2% for A7 and 1.5% for C10, which proves that $\Delta p/p$ is still increasing with growth inhibition. If we now compare two other deposits obtained under different plating conditions, but leading to the same value of $\Delta p/p = 2.6\%$, it may be seen on Fig. 3 that A6 and B7 exhibit a quite similar surface morphology. It thus appears to be well founded to express our subsequent results in terms of $\Delta p/p$ rather than in terms of surface morphology to characterize growth inhibition.

3.4. Weight increase of silver deposits

Experimental values of $\Delta p/p$ versus α_{HA^-} are plotted on Fig. 4 for all deposits of Table 1. Four curves are obtained, each of them showing the same shape as depicted in Fig. 5b of the work by Amblard et al. [8], but with a shift towards lower incorporation rates for more dilute $AgNO_3$ solutions.

From these curves it is now obvious that $\Delta p/p$ only depends on α_{HA^-} provided that the $AgNO_3$ concentration is kept constant. Conversely, if

α_{HA^-} is kept constant, $\Delta p/p$ is higher for more concentrated $AgNO_3$ solutions, which means smoother Ag plates. This behaviour strongly militates in favour of our assumption according to which a complex such as Ag(HA) could be responsible for the growth inhibition. As a matter of fact, if such a complex is formed in bulk solution according to the equilibrium

$$Ag^+ + HA^- \rightleftharpoons Ag(HA) \qquad (1)$$
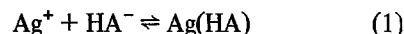
the growth inhibition, and then $\Delta p/p$, should depend on the concentration of Ag(HA) only, i.e. on the product $K_F \alpha_{Ag^+} \alpha_{HA^-}$, where
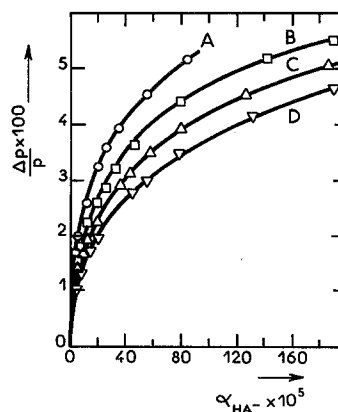

Fig. 4. Experimental values of $\Delta p/p$ vs α_{HA^-} for all deposits of Table 1. Each curve corresponds to a definite $AgNO_3$ concentration: $A = 0.2$ M, $B = 0.1$ M, $C = 0.075$ M and $D = 0.05$ M.
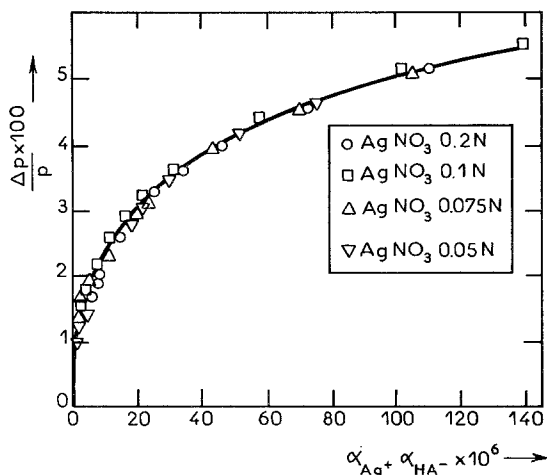
Fig. 5. Experimental values of $\Delta p/p$ vs $\alpha_{Ag^+}\alpha_{HA^-}$ for all deposits of Table 1.

Fig. 6. Logarithmic plot of the four curves of Fig. 4 restricted to large values of α_{HA^-}.

K_F is the constant of formation of Ag(HA). We could explain in this way that, for a given AgNO₃ concentration (α_{Ag^+} nearly constant), HA⁻ appears to be the active component in the solution. Conversely, if α_{HA^-} has a given value, then α_{Ag^+} (or the related AgNO₃ concentration) is the sole relevant parameter governing the growth inhibition.

What happens now when α_{Ag^+} and α_{HA^-} are both varying? Under the assumption that Ag(HA) is the unique growth inhibitor, then the dependence of $\Delta p/p$ vs [Ag(HA)] must be expressed by a unique curve for the four series of Ag electrodeposits studied here. This is clearly evidenced by Fig. 5 where [Ag(HA)] is expressed by the product $\alpha_{Ag^+}\alpha_{HA^-}$. In order to determine $\alpha_{Ag^+} = \gamma_{Ag^+}C_{Ag^+}$, we must calculate the activity coefficient γ_{Ag^+} for different ionic strengths using Guggenheim's relation [21]

$$\log \gamma_I = \frac{-0.50916(I)^{1/2}}{1 + (I)^{1/2}} + \lambda I \qquad (2)$$

Here λ was determined from experimental γ_{Ag^+} values [22] and was found to be equal to -0.121 for I values ranging from 0.05 to 0.90. We have also taken into account the limited formation of ion pairs between Ag⁺ and NO₃⁻ [23].

3.5. Ag(HA) as the relevant parameter for growth inhibition
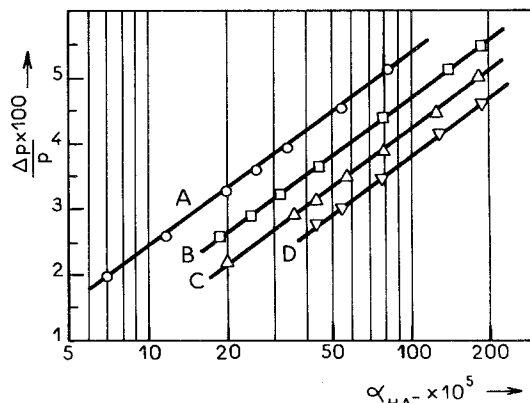
That a 1:1 complex between Ag⁺ and HA⁻ is the

active component governing growth inhibition can be derived from a more rigorous method. We have observed that every $\Delta p/p$ vs α_{HA^-} curve is in fair congruence with a simple relation taking the form

$$\frac{\Delta p}{p} = a + b \log \alpha_{HA^-} \qquad (3)$$

for large values of α_{HA^-}. This is obvious on Fig. 6 where the four curves of Fig. 4 are plotted on a logarithmic scale. This plot gives four parallel straight lines, which can be understood in the following way. Let us assume that Equation 3 is a particular case of a more general empirical relation such as

$$\frac{\Delta p}{p} = A + B \log \alpha_C \qquad (4)$$

where α_C corresponds to the activity of the efficient component C responsible for growth inhibition. Such an active component might be a complex between one Ag⁺ and n monoanions HA⁻ resulting from

$$Ag^+ + n(HA)^- \rightleftharpoons [Ag(HA)_n]^{(n-1)-} \qquad (5)$$
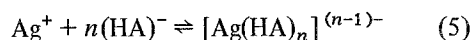
It follows that

$$\alpha_C = K_F \alpha_{Ag^+}\alpha_{HA^-}^n \qquad (6)$$

and, combining Equations 4 and 6 we have

$$\frac{\Delta p}{p} = A_1 + B \log \alpha_{Ag^+} + nB \log \alpha_{HA^-} \qquad (7)$$

with $A_1 = A + B \log K_F$.

It is obvious that, under the condition $\alpha_{Ag^+} =$

constant, Equation 7 falls into Equation 3, but in the general case Equation 7 expresses the dependence of $\Delta p/p$ vs both α_{Ag^+} and α_{HA^-}.

From our experimental data concerning the four series of deposits, we found a very good agreement between Equation 7 and the observed dependence of $\Delta p/p$ vs both parameters ($R^2 = 0.9959$). A multiple linear regression method leads to the numerical relation

$$\frac{\Delta p}{p} = 0.165 + 0.029 \log \alpha_{Ag^+} + 0.029 \log \alpha_{HA^-}$$

$$(8)$$

from which the coordination number n was found to be equal to unity.

4. Conclusions

A systematic study of Ag electrodeposits obtained from various $AgNO_3$ solutions containing tartaric acid has enabled us to show which chemical entity is responsible for the growth inhibition: the effect starts with the formation in the bulk of a 1:1 complex between Ag^+ and tartaric monoanions HA^-. Because of its neutrality this complex has to be transported towards the cathode by convective diffusion. In so far as it is heavily incorporated into the metallic plate, it must be strongly adsorbed on the cathodic surface. The growth inhibition may be characterized by the weight increase $\Delta p/p$ as well as by structural features such as grain size or superficial roughness. All these parameters are shown to depend only on the complex concentration [Ag(HA)].

A further step towards a full elucidation of the mechanism of growth inhibition will demand additional data throwing some light on the way such a complex may desorb from the cathodic surface. This may be achieved by varying the current density and keeping the concentration

of [Ag(HA)] constant so as to compare the inhibiting effect of the complex for various silver growth rates.

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