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Influence of tartaric acid on the electrodeposition of silver from binary water + dioxane $AgNO_3$ solutions

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Abstract

Silver electrodeposits prepared from $AgNO_3$ solutions never give compact, smooth plates unless an organic additive, such as tartaric acid (H_2A), is used as growth inhibitor. It was shown previously that the relevant chemical entity controlling growth inhibition is the bulk concentration of a neutral associate Ag(HA) formed in the solution between Ag^+ and tartaric monoanions HA^-. In the present work we extend this investigation to mixed water + dioxane solvent systems where the addition of dioxane, affecting the formation constant of Ag(HA), changes the bulk concentration of this associate. It was found that the associate Ag(HA) also formed in water + dioxane solvent systems is the active component in the solution governing the growth inhibition. On the concentration of this associate most of the structural features of Ag deposits (e.g., the grain size, the superficial roughness and the degree of the preferred orientation ⟨1 1 0⟩) depend.

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]. Many substances, mainly organic, are used as additives in plating solutions to improve certain physical and/or mechanical properties of the electroplated silver. Tartaric acid ($H_2C_4H_4O_6$ abbreviated as H_2A), whose smoothing effect has long been known [9], is among the most effective growth inhibitors [5–11].

We have shown in previous work that for silver deposits prepared from an aqueous 0.5 M $AgNO_3$ solution, the relevant parameter hindering dendritic growth was the concentration of tartaric monoanions HA^-, regardless of the concentrations of the other ionic and nonionic entities in the solution [8]. The latter species have a concentration significantly different [12]. Subsequent work in aqueous solutions with varying $AgNO_3$ concentrations showed that the relevant chemical entity controlling growth inhibition is the bulk concentration of a neutral associate Ag(HA) [13, 14]. It was decided to extend this investigation to mixed water + dioxane solvent systems where the addition of dioxane, affecting the formation constant of Ag(HA), changes the bulk concentration of this associate. The binary water + dioxane solvent mixtures are well known as popular media for electrochemical studies. Apart from the wide range of dielectric constant that can be achieved by the addition of dioxane, these solvent systems preserve, to a considerable degree, the excellent solvent properties of dioxane for many organic substances. In addition, the presence of water assures the solubility of various inorganic salts. Consequently, the production of smooth, compact and coherent silver electrodeposits from such solvent media, where many organic additives can be brought into solution, is of considerable importance.

2. Experimental details

The experimental conditions and procedure for the preparation of the deposits were described previously [13, 14]. Both cathode and anode were made of high purity silver (99.999% Matthey Chemicals). Doubly distilled water, $AgNO_3$ (Merck p.a.), tartaric acid (*L*(+) Carlo Erba RP-ACS) and 1 M HNO_3 solution (Merck Titrisol) were used for the preparation of the solutions. Carlo Erba 1,4-dioxane (>99% (v/v), b.p. 101) was further purified as described previously [15].

The surface morphology was examined by means of a Jeol JSM-840A scanning electron microscope and the roughness was determined with a Perthen C5D (no.

6250203) profilograph connected to a microtracer (RHT 6-250) via a drive unit (SPVK, no. 6720417). For the automatic acquisition of roughness data, the profilograph was interfaced to a personal computer via a A–D/D–A card. A Philips PW 1077 X-ray diffractometer (MoK_α) was used for studying the crystal structure of the deposits. The pH of the solutions was determined by using a Denver (model 50) digital pH-meter (accuracy ±0.001 pH units) connected to the electrode pair glass electrode (Ingold U262-S7/120)/reference electrode (Ingold, 363-S7/120). A salt bridge of saturated KNO_3 solution insulated the reference electrode from the measured solution.

3. Results and discussion

3.1. *General effect of tartaric acid, H_2A*

Six series of electrodeposits were studied, each series corresponding to a definite $AgNO_3$ concentration and dioxane content. The main composition parameters for every case are listed in Table 1. The activities α_{HA^-} of HA^- were calculated by adapting a general method for polyprotic acids [16–18] to diprotic ones. Values of the dissociation constants K_1 and K_2 of tartaric acid in water and water + dioxane solvent systems were taken from literature [19, 20].

Some silver plates were prepared from $AgNO_3$ solutions without tartaric acid, in order to detect any inhibiting effect of dioxane on the silver growth. The solutions contained 0.1 or 0.2 M $AgNO_3$, 10% or 20% (v/v) dioxane and HNO_3 ranging from 0.05 to 0.6 M. It was found that only solutions with HNO_3 concentration greater than 0.5 M led to deposits with good adherence to the substrate. However the roughness of these deposits was relatively high. This behaviour is similar to that observed in the case of silver deposits prepared from aqueous $AgNO_3$ solutions [21]. The experimental weight of these deposits obtained from solutions with HNO_3 concentration greater than 0.5 M HNO_3 was found to be equal to the theoretical weight, p, expected from Faraday's law. So, in the absence of tartaric acid, dioxane does not participate in any electrochemical reactions during the deposition process. Smooth and coherent silver deposits can be obtained from $AgNO_3$ solutions in water + dioxane mixtures only in the presence of tartaric acid.

X-ray diffraction diagrams (XRD) of the deposits showed that all the plates presented preferred orientation with a $\langle 1\ 1\ 0 \rangle$ texture axis. This effect was more pronounced for the smoother, coherent deposits. The determination of the texture axis results from the comparison of the XRD diagrams of the deposits with that of randomly oriented silver powder [22, 23]. The preferred orientation $\langle 1\ 1\ 0 \rangle$ is readily detected from the increase in the intensities of (2 2 0) and (4 4 0) reflections comparatively to the respective intensities of the silver powder. Figure 1 shows as an example the XRD diagram of a deposit (A2) with strong preferred orientation in comparison to the XRD diagram of silver powder free from any preferred orientation.

The $\langle 1\ 1\ 0 \rangle$ texture can quantitatively be expressed by a parameter, Q_{110}, known as the '*degree of preferred orientation*', which can experimentally be determined from XRD diagrams [22, 23]. This parameter is defined by the relation:

$$Q_{110} = m_{110} R_{220} \tag{1}$$

m_{110} being the multiplicity of $\{1\ 1\ 0\}$ planes and R_{220}, the ratio of the integrated intensities of (2 2 0) reflec-

Table 1. Composition of $AgNO_3$ + tartaric acid (H_2A) solutions in binary water + 1,4-dioxane solvent mixtures that give compact silver electrodeposits. $[H_2A]$ = 0.015 M

(a) 0.2 M $AgNO_3$, 10% (v/v) dioxane				(b) 0.2 M $AgNO_3$, 20% (v/v) dioxane				(c) 0.2 M $AgNO_3$, 30% (v/v) dioxane			
Deposit	$[HNO_3]$	pH	$\alpha_{HA^-} \times 10^5$	Deposit	$[HNO_3]$	pH	$\alpha_{HA^-} \times 10^5$	Deposit	$[HNO_3]$	pH	$\alpha_{HA^-} \times 10^5$
A1	0.02	1.804	49.9	B1	0.02	1.882	33.20	C1	0.02	1.935	19.10
A2	0.03	1.680	38.0	B2	0.03	1.752	24.90	C2	0.03	1.803	14.20
A3	0.04	1.584	30.7	B3	0.04	1.652	19.90	C3	0.04	1.705	11.40
A4	0.05	1.509	25.9	B4	0.05	1.574	16.70	C4	0.05	1.631	9.59
A5	0.06	1.448	22.6	B5	0.06	1.512	14.50	C5	0.06	1.571	8.37
A6	0.08	1.350	18.1	B6	0.08	1.411	11.50	C6	0.08	1.473	6.70
A7	0.10	1.271	15.2	B7	0.10	1.331	9.59	C7	0.10	1.392	5.55

(d) 0.1 M $AgNO_3$, 10% (v/v) dioxane				(e) 0.1 M $AgNO_3$, 20% (v/v) dioxane				(f) 0.1 M $AgNO_3$, 30% (v/v) dioxane			
Deposit	$[HNO_3]$	pH	$\alpha_{HA^-} \times 10^5$	Deposit	$[HNO_3]$	pH	$\alpha_{HA^-} \times 10^5$	Deposit	$[HNO_3]$	pH	$\alpha_{HA^-} \times 10^5$
D1	0.02	1.867	57.4	E1	0.02	1.937	37.7	F1	0.02	1.973	20.80
D2	0.03	1.720	41.6	E2	0.03	1.796	27.5	F2	0.03	1.843	15.60
D3	0.04	1.611	32.6	E3	0.04	1.690	21.7	F3	0.04	1.740	12.30
D4	0.05	1.527	27.0	E4	0.05	1.609	18.1	F4	0.05	1.658	10.20
D5	0.06	1.460	23.2	E5	0.06	1.545	15.6	F5	0.06	1.591	8.76
D6	0.08	1.354	18.3	E6	0.08	1.447	12.5	F6	0.08	1.489	6.94
D7	0.10	1.271	15.2	E7	0.10	1.371	10.5	F7	0.10	1.413	5.83

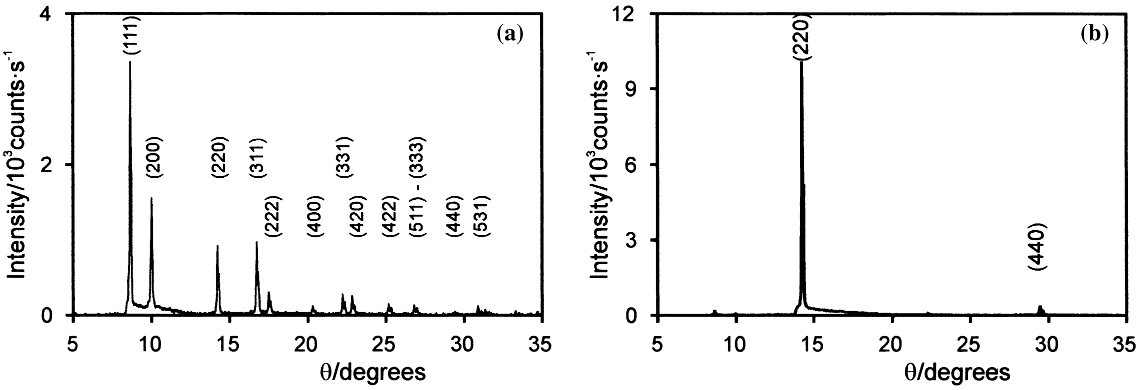


Fig. 1. Comparison of XRD diagrams between a randomly oriented Ag powder and an Ag deposit. (a) Randomly oriented silver powder, (b) deposit A2 (0.2 M $AgNO_3$, 0.015 M H_2A, 0.03 M HNO_3 in water + dioxane mixture containing 10% dioxane).

tions corresponding to the deposit (I_{220}) and to the randomly oriented silver powder (I_R), respectively. Thus we have:

$$R_{220} = \frac{I_{220}}{I_R} \tag{2}$$

So, the intensity of (2 2 0) lines of XRD diagrams is a measure of Q_{110}. Evidently, in the study of a single $\langle h\,k\,l \rangle$ texture axis, the use of the ratio I_{hkl}/I_R instead of Q_{hkl} reach to identical conclusions. However, here we used Equation 1, which permits the comparison of two or more texture axes with different multiplicities [22].

3.2. *Effect of monoanion activity, α_{HA^-}*

Examination of the plates of each series revealed the same dependency between α_{HA^-} and surface morphology as depicted in aqueous $AgNO_3$ + tartaric acid solutions [14], i.e. the greater is α_{HA^-} the smoother is the corresponding deposit. It was also found that α_{HA^-} affects the parameter Q_{110} of the deposits. Indeed, in each series, the intensity of the (2 2 0) line increased with increasing α_{HA^-}. Figure 2 illustrates such a tendency for two deposits of series (e). Both deposits were prepared from a 0.1 M $AgNO_3$ in 20% (v/v) dioxane + water solution but E1 corresponds to a value of α_{HA^-} 3.6 times greater than in the E7 case. From Figure 2 it results that E1 is much smoother and presents a greater degree of preferred orientation than E7.

In all cases, it was found that the experimental weight of the deposits was systematically greater than the theoretical one. This effect was attributed previously to the incorporation of organic molecule into the plate [8, 13, 14]. It is worth noting that, 75 years ago, Fuseya and Murata [6] showed for the first time that the excess weight Δp is due to the incorporation of tartaric acid molecules into the silver deposit.

In each series of deposits, the ratio $\Delta p/p$ increased with increasing values of α_{HA^-}. For example, a measurement of $\Delta p/p$ for both deposits of Figure 2 gives 4.8% for E1 and 3.2% for E7.

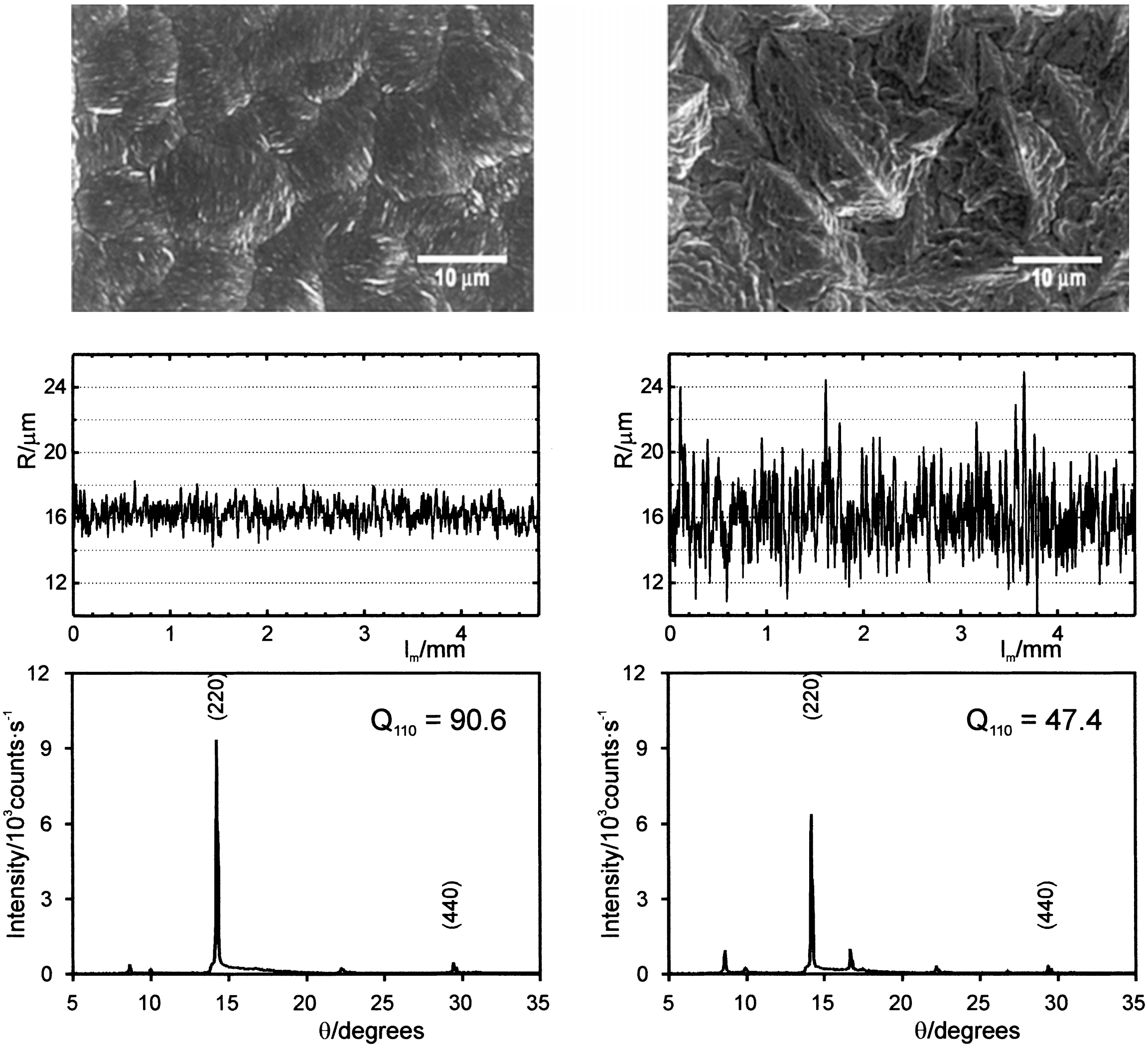
3.3. *Effect of $AgNO_3$ concentration*

To clarify the role of silver nitrate concentration, [$AgNO_3$], on the growth inhibition, [$AgNO_3$] was varied with α_{HA^-} and dioxane content constant. In Figure 3 two deposits (A7 and D7) prepared from solutions with the same α_{HA^-} and dioxane content but with different [$AgNO_3$], 0.2 and 0.1 M respectively, are compared. Growth inhibition depends equally on [$AgNO_3$]; more dilute solutions give less smooth deposits. This result was not unexpected since dilution, in aqueous $AgNO_3$ solutions (without tartaric acid), favours dendritic growth [1–3, 7]. The same conclusion holds even in the presence of an efficient growth inhibitor such as tartaric acid.

It was also found that [$AgNO_3$] affects the degree of preferred orientation $\langle 1\ 1\ 0 \rangle$ as well as the ratio $\Delta p/p$ of the resulting deposits. In all cases of deposits prepared from solution with the same α_{HA^-} and dioxane content, the intensity of (2 2 0) reflections of the corresponding XRD diagrams increased with increasing [$AgNO_3$]. Figure 3 illustrates this behaviour. Concerning the dependency of $\Delta p/p$ on the silver nitrate concentration, this study showed that $\Delta p/p$ was an increasing function of [$AgNO_3$]. For example, the values of $\Delta p/p$ for the deposits of Figure 3 were 3.7% for A7 and 2.9% for D7.

3.4. *Effect of 1,4-dioxane content*

The effect of dioxane content on the properties of Ag deposits was studied by preparing plates from electrolytic solutions with the same values of α_{HA^-} and [$AgNO_3$] but with different dioxane concentration. It was found that, in the presence of tartaric acid, an increase in dioxane content increased the degree of preferred orientation and the ratio $\Delta p/p$, but decreased the roughness of the deposits. A comparison between the properties of the plates F2 (Figure 4) and D7 (Figure 3) reveals this behaviour. These deposits were prepared from solutions with the same $AgNO_3$ concentration (0.1 M) and nearly the same activity α_{HA^-} but with different dioxane content (30% and 10% for F2 and D7, respectively).



(a) (b)

Fig. 2. Influence of monoanion activity on surface morphology (SEM micrographs), roughness (curves) and degree of preferred orientation ⟨1 1 0⟩ (XRD diagrams) of two deposits. [$AgNO_3$] = 0.1 M in water + dioxane mixture (20% dioxane). (a) Deposit E1 ($\alpha_{HA^-} = 37.7 \times 10^{-5}$ M), (b) deposit E7 ($\alpha_{HA^-} = 10.5 \times 10^{-5}$ M).

3.5. *Role of weight increase of silver deposits on the growth inhibition*

In all cases it was found that the ratio $\Delta p/p$ is closely related to structural parameters such as morphology, surface roughness and degree of preferred orientation ⟨1 1 0⟩. Greater values of $\Delta p/p$ mean smoother deposits with finer grain size and higher degree of preferred orientation.

On the other hand, deposits with quite similar surface morphology, roughness and degree of preferred orientation ⟨1 1 0⟩ exhibit nearly the same values of $\Delta p/p$. Indeed, in Figure 5 a comparison between the properties of two deposits (A4 and B5) obtained under different plating conditions but having almost equal values of $\Delta p/p$ illustrates that they exhibit a quite similar surface morphology, roughness and degree of preferred orientation ⟨1 1 0⟩. It thus appears that the quantitative parameter $\Delta p/p$ characterizes the global effect of growth inhibition.

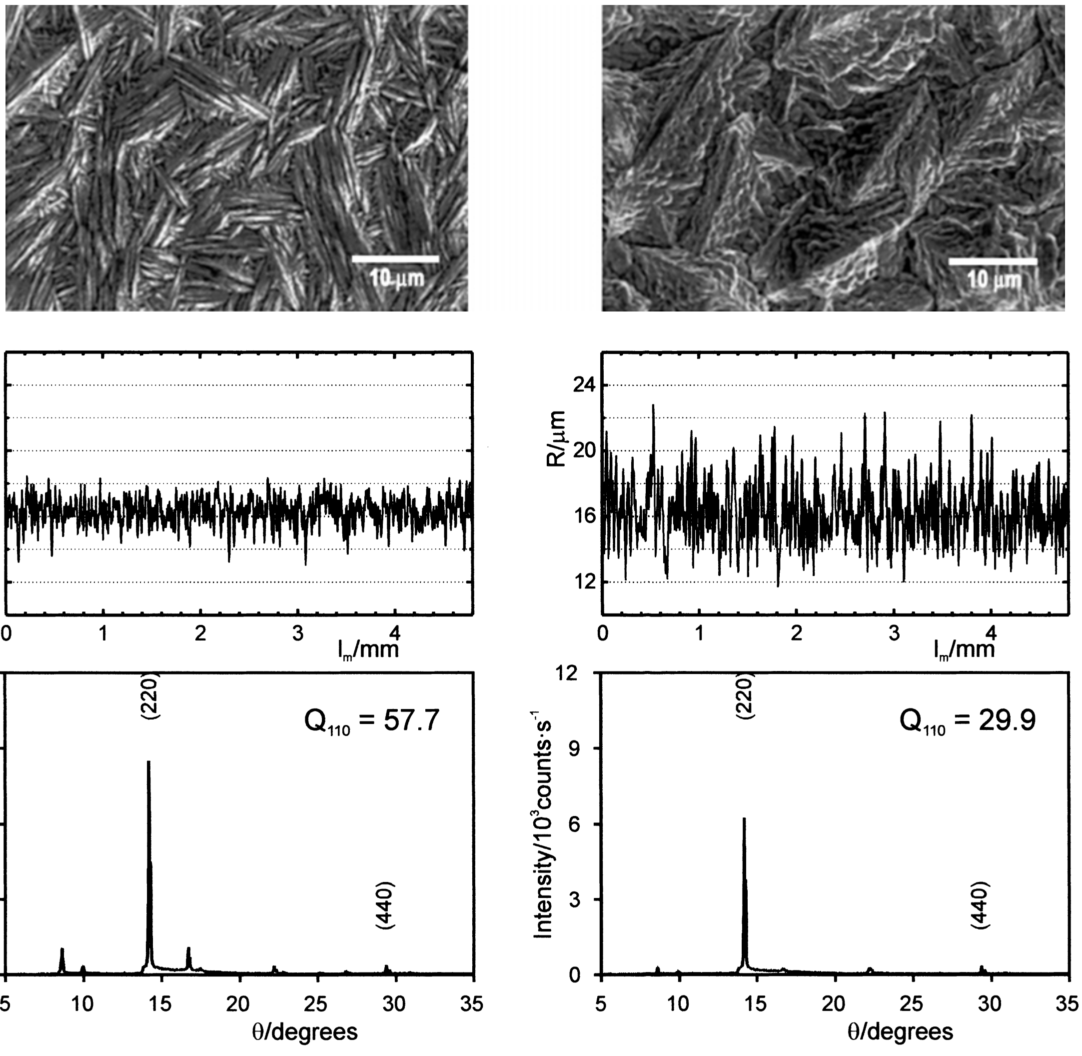
Experimental values of $\Delta p/p$ against α_{HA^-} are plotted on Figure 6 for all deposits of Table 1. Each of the three plots corresponds to constant dioxane concentration. The two curves, are for different $AgNO_3$ concentrations. At each solvent composition a shift towards lower $\Delta p/p$ values for more dilute $AgNO_3$ solutions occurred and for increasing dioxane content the curves shifted toward higher $\Delta p/p$ values.

This behaviour could be explained by assuming that an associate of the form Ag(HA) could be responsible for growth inhibition. If such an associate is formed in bulk solution, the growth inhibition, and then $\Delta p/p$, should depend only on the activity, α_c, of Ag(HA). The activity α_c is expressed by:

$$\alpha_c = K_F \alpha_{Ag^+} \alpha_{HA^-} \tag{3}$$

where K_F is the equilibrium constant:

$$Ag^+ + HA^- \rightleftharpoons Ag(HA) \tag{4}$$



(a) **(b)**

Fig. 3. Influence of $AgNO_3$ concentration on surface morphology (SEM micrographs), roughness (curves) and degree of preferred orientation $\langle 1\ 1\ 0\rangle$ (XRD diagrams) of two deposits prepared from solutions in water + dioxane mixture (10% dioxane). (a) Deposit A7 ($[AgNO_3]$ = 0.2 M, $\alpha_{HA^-} = 15.2 \times 10^{-5}$ M, $\Delta p/p$ = 3.7%), (b) deposit D7 ($[AgNO_3]$ = 0.1 M, $\alpha_{HA^-} = 15.2 \times 10^{-5}$ M, $\Delta p/p$ = 2.9%).

The formation constant, K_F, of Ag(HA), depending on the dielectric constant of the solution, may remain invariable provided that the solvent composition is constant.

Equation 3 shows why, in each series of deposits where the solvent composition remains constant while α_{Ag^+} is nearly constant, HA^- appears to be the active component in the solution. In contrast, if α_{HA^-} has a given value, then α_{Ag^+} (or the related $[AgNO_3]$) is the sole relevant parameter governing growth inhibition.

What happens now if α_{Ag^+} and α_{HA^-} are both varying? Under the hypothesis that Ag(HA) is the unique growth inhibitor, the dependence of $\Delta p/p$ against the activity of Ag(HA), α_c, must be expressed by a unique curve for the two series of Ag deposits prepared in each solvent composition. This is clearly shown by Figure 7, where the product $\alpha_{Ag^+}\alpha_{HA^-}$ is used to express α_c.

In the determination of the activities $\alpha_i = \gamma_i C_i$ of various ionic species of valence z_i, the activity coefficient γ_i was calculated from Davies' relation [24]:

$$\log \gamma_i = \frac{-Az_i^2\sqrt{I}}{1+\sqrt{I}} + 0.1z_i^2 I \qquad (5)$$

A being the Debye–Hückel constant, the values of which depend on the temperature T and the dielectric constant D of the solvent medium [25]. In the calculation of γ_i, the values of D were taken from [16]. Concerning the ionic strength I of the solution, a simple calculation gives:

$$I = [AgNO_3] + [H^+] + [A^{2-}] \qquad (6)$$

The values of I can be calculated by means of an iterative method described previously [17].

In order to test the precision of the results of this investigation, silver deposits were prepared from aqueous $AgNO_3 + H_2A$ solutions. The values of $\Delta p/p$ are reported and compared to the data of our previous work [14] in Figure 7; the agreement is excellent.

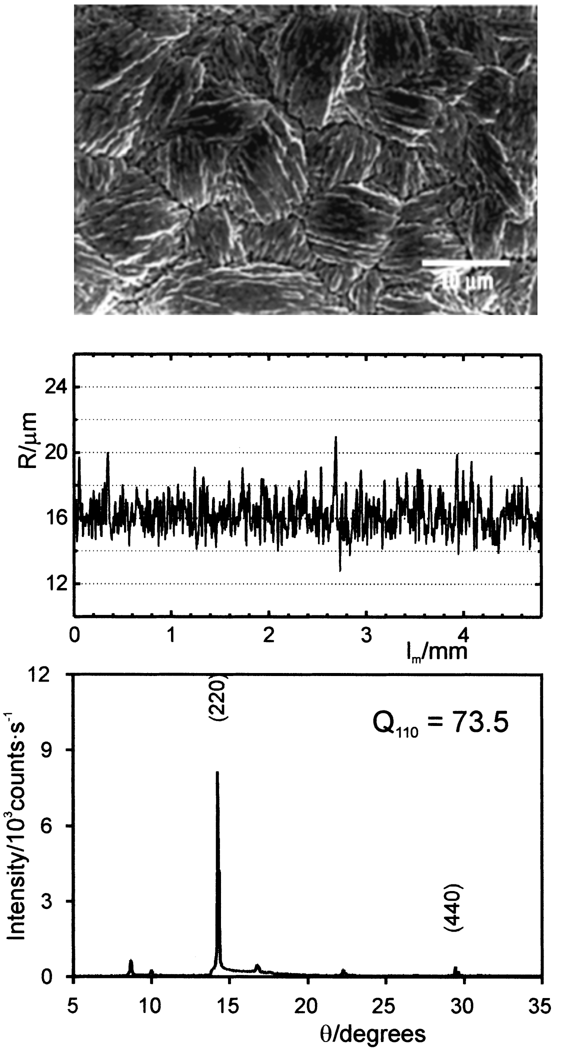


Fig. 4. Surface morphology (SEM micrographs), roughness (curves) and degree of preferred orientation ⟨1 1 0⟩ (XRD diagrams) of F2 deposit ($[AgNO_3] = 0.1$ M, $\alpha_{HA^-} = 15.6 \times 10^{-5}$ M, dioxane content = 30% v/v, $\Delta p/p = 4.48\%$).

The graphs of Figure 7 show that at constant solvent composition, $\Delta p/p$ is an increasing function of the product $\alpha_{Ag^+}\alpha_{HA^-}$. However, as the dioxane content increases, the corresponding graphs shift towards higher values of $\Delta p/p$.

This behaviour may be explained under the assumption that the parameter controlling the growth inhibition is the bulk activity α_c of the associate Ag(HA). The addition of dioxane, lowering the dielectric constant D of the solvent medium [16], increases the ionic attraction of the various ionic species of opposite charge. Thus, the formation constant of Ag(HA) increases with increasing dioxane content. Consequently, at constant values of the product $\alpha_{Ag^+}\alpha_{HA^-}$, the bulk activity α_c increases with decreasing values of D.

3.6. *Ag(HA) as the relevant parameter for growth inhibition*

As in the case of aqueous $AgNO_3 + H_2A$ solutions [14], in each series of deposits it was found that the corresponding $\Delta p/p$ against α_{HA^-} curve can be fitted by a least squares technique to a simple logarithmic relation of the form ($R^2 > 0.998$):

$$\frac{\Delta p}{p} = a + b \log \alpha_{HA^-} \tag{7}$$

On the assumption that an associate formed between Ag^+ and HA^- is the active component in the solution controlling growth inhibition, Equation 7 may be assumed to be a particular case of a more general empirical relation of the form:

$$\frac{\Delta p}{p} = A + B \log \alpha_c \tag{8}$$

where α_c corresponds to the activity of the component responsible for growth inhibition. Such a component might be an associate between one Ag^+ and n monoanions HA^-, according to the following equilibrium:

$$Ag^+ + n(HA^-) \rightleftharpoons [Ag(HA)_n]^{(n-1)^-} \tag{9}$$

It follows then that

$$\alpha_c = K_F(\alpha_{Ag^+})(\alpha^n_{HA^-}) \tag{10}$$

Combination of Equations 8 and 10 gives

$$\frac{\Delta p}{p} = A_0 + B_1 \log(\alpha_{Ag^+}) + B_2 \log(\alpha_{HA^-}) \tag{11}$$

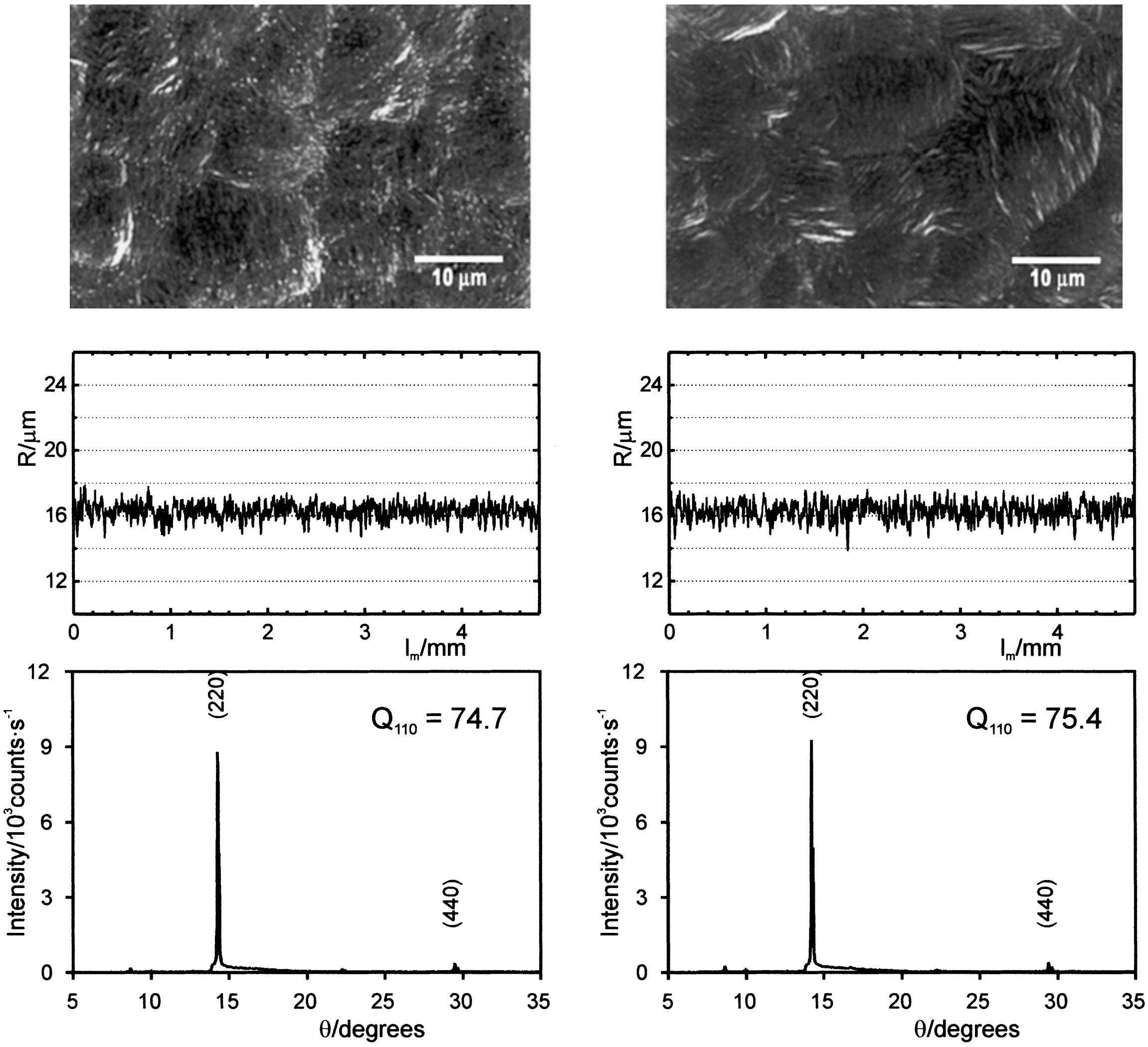
where $A_0 = A + B \log K_F$, $B_1 = B$ and $B_2 = nB$.

It is obvious that, in each series of deposits where α_{Ag^+} and dioxane content remain constant (K_F = constant), Equation 11 becomes Equation 7.

Equation 11 having the form

$$\frac{\Delta p}{p} = A_0 + B_1 X_1 + B_2 X_2$$

predicts a linear dependence of $\Delta p/p$ against X_1 and X_2. Alternatively, the experimental confirmation of such a correlation supports the assumption that the active component in the solution controlling growth inhibition is a complex $[Ag(HA)_n]^{(n-1)^-}$. In such a case, the coordination number can be determined from the ratio of the coefficients B_1 and B_2. Indeed, at each solvent composition studied, it was found that Equation 11 fits the experimental data very successfully ($R^2 \geqslant 0.9983$). The coefficients A_0, B_1 and B_2 determined by a multiple linear regression method are listed in Table 2 along with the corresponding values of R^2. The values of Table 2 show that n is nearly equal to unity for all solvent compositions. Thus, by using a more rigorous method it was detected that the active component, in the bulk solution, on the growth inhibition is a 1:1 associate between Ag^+ and HA^-.



(a) **(b)**

Fig. 5. Surface morphology (SEM micrographs), roughness (curves) and degree of preferred orientation ⟨1 1 0⟩ (XRD diagrams) of two deposits exhibiting equal values of $\Delta p/p$ but prepared from different solutions. (a) Deposit A4 ($[AgNO_3]$ = 0.2 M, $\alpha_{HA^-} = 25.9 \times 10^{-5}$ M, dioxane content = 10% v/v, $\Delta p/p$ = 4.33%), (b) deposit B5 ($[AgNO_3]$ = 0.2 M, $\alpha_{HA^-} = 14.5 \times 10^{-5}$ M, dioxane content = 20% v/v, $\Delta p/p$ = 4.36%).

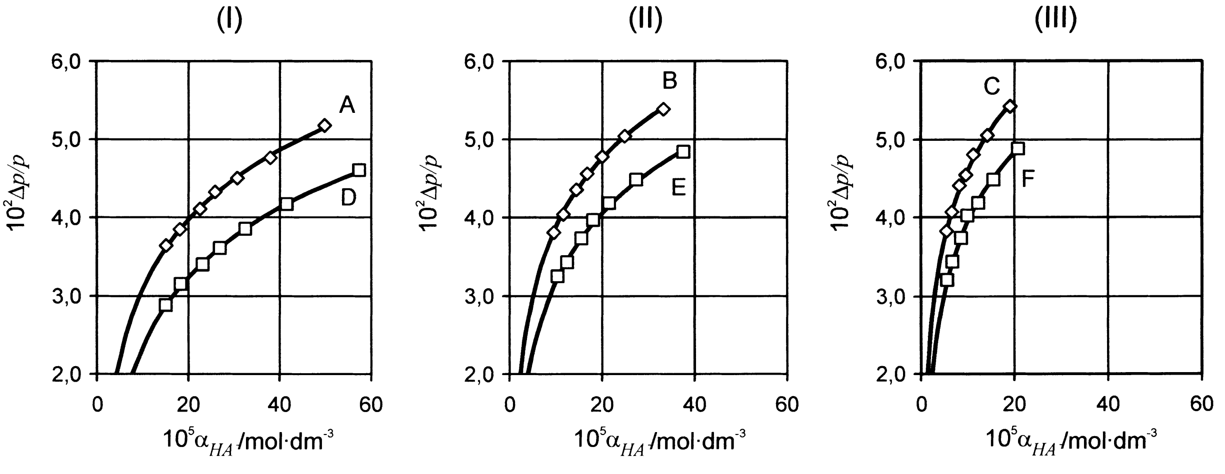


Fig. 6. Variation of $\Delta p/p$ with α_{HA^-} for all deposits of Table 1. Each curve corresponds to a definite $AgNO_3$ concentration and dioxane content. (I) 10% dioxane: A = 0.2 M $AgNO_3$, D = 0.1 M $AgNO_3$. (II) 20% dioxane: B = 0.2 M $AgNO_3$, E = 0.1 M $AgNO_3$. (III) 30% dioxane: C = 0.2 M $AgNO_3$, F = 0.1 M $AgNO_3$.

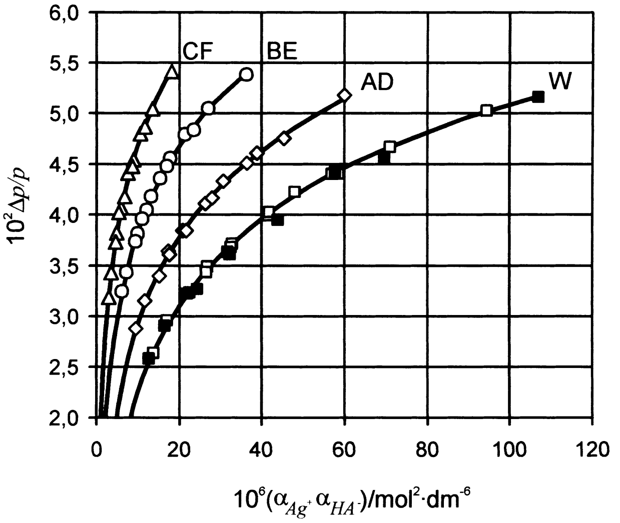


Fig. 7. Variation of $\Delta p/p$ with $\alpha_{Ag^+}\alpha_{HA^-}$. Each curve corresponds to a definite dioxane content. (W) aqueous solutions: (■) = data from Ref. [14]; (AD) 10% dioxane (series (a) and (d)); (BE) 20% dioxane (series (b) and (e)); (CF) 30% dioxane (series (c) and (f)).

Table 2. Coefficients of Equation 11, coordination number n and coefficient of determination R^2 corresponding to various water + 1,4-dioxane solvent mixtures

% (v/v) dioxane	A_0	B_1	B_2	n	R^2
10	0.1707(17)	0.0291(6)	0.0280(4)	0.96	0.9983
20	0.1786(13)	0.0288(5)	0.0279(3)	0.97	0.9990
30	0.1884(19)	0.0291(6)	0.0281(4)	0.97	0.9983

Given that $n = 1$, Equation 9 can be written as

$$\frac{\Delta p}{p} = A_0 + B\log(\alpha_{Ag^+}\alpha_{HA^-}) \qquad (12)$$

Equation 12 predicts a linear relation between $\Delta p/p$ and $\log(\alpha_{Ag^+}\alpha_{HA^-})$ at each solvent composition, where $A_0 = A + B\log K_F$ = constant. As the dioxane content increases, K_F and A_0 also increase and this fact may result in a parallel displacement of the corresponding line toward higher $\Delta p/p$ values. Indeed, in all solvent mixtures used, the expected linear relationships between $\Delta p/p$ and $\log(\alpha_{Ag^+}\alpha_{HA^-})$ were observed; the parallel straight lines are given in Figure 8.

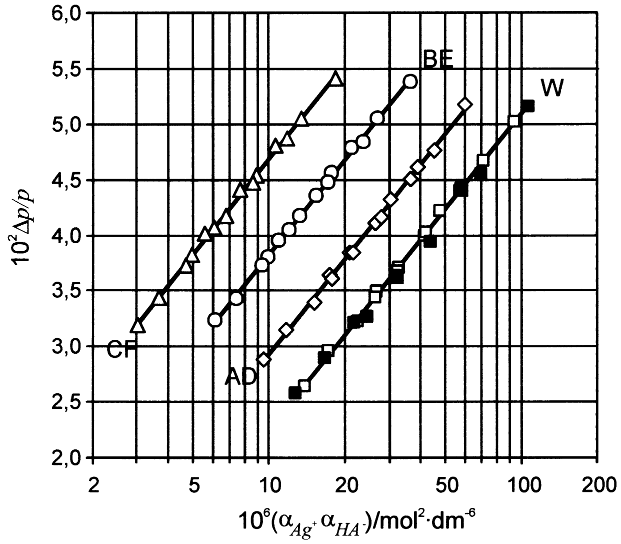
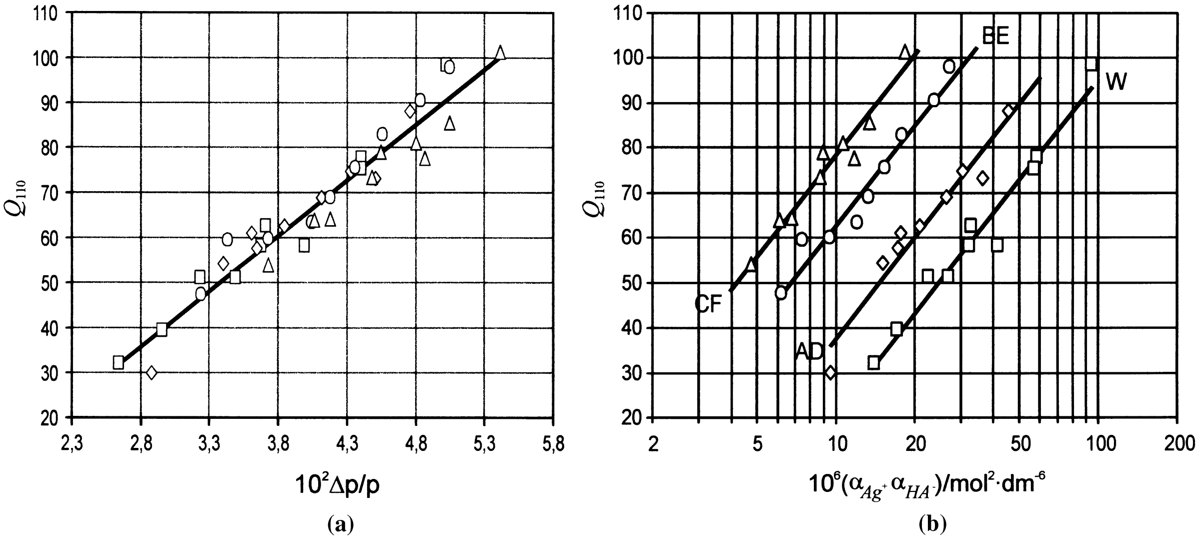


Fig. 8. Logarithmic plot of the four curves of Figure 7.

3.7. *Ag(HA) as the relevant parameter for the structural features of the deposits*

To establish a quantitative correlation between growth inhibition and the structural features of the deposits, the values of a quantitative structural parameter such as Q_{110} were plotted against $\Delta p/p$ (Figure 9(a)). For all the series of deposits, a unique straight line with positive slope was obtained showing a clear correlation between growth inhibition, quantitatively expressed by $\Delta p/p$, and Q_{110}.



(a)

(b)

Fig. 9. Variation of Q_{110} with $\Delta p/p$ (a) and $\alpha_{Ag^+}\alpha_{HA^-}$ (b). (W) aqueous solutions; (AD) 10% dioxane; (BE) 20% dioxane; (CF) 30% dioxane.

Furthermore, taking into account the linear relation between $\Delta p/p$ and $\log \alpha_c$, an analogous correlation between Q_{110} and $\log \alpha_c$ is expected. Indeed, the graphs of Figure 9(b) prove such a correlation. The similarity between the plots of 9(b) and 8 provides further experimental evidence that Ag(HA) is the active component in the solution also controlling the structural features of the deposits.

4. Conclusions

A systematic study of Ag electrodeposits obtained from $AgNO_3$ + tartaric acid (H_2A) solutions in binary water + dioxane solvent systems showed that it is possible to obtain compact and coherent silver deposits from such solvent media. In these media, a similar behaviour to that observed previously in aqueous $AgNO_3 + H_2A$ solutions was observed. Thus, it was elucidated that an associate Ag(HA) is the active component in the solution governing growth inhibition. Due to its electrical neutrality, Ag(HA) has to be transported towards the cathode by convection. The growth inhibition may be characterized by the ratio $\Delta p/p$, as well as by structural features such as grain size, surface roughness and Q_{110}. It was proved that all these parameters depend only on the concentration of Ag(HA). Consequently, the structural features of the deposits can be modified by changing the concentration of Ag(HA) in the bulk solution. The Ag(HA) concentration can be easily controlled by: (a) modifying the concentrations of $AgNO_3$ or H_2A, (b) adjusting the pH of the bulk solution and (c) modifying the composition of the mixed solvent system.

It is worth noting that the ability to plate from mixed water + organic solvent systems, where various water-insoluble organic additives can be brought into solution, is of considerable importance. Finally, the results of this investigation are of environmental interest; $AgNO_3 + H_2A$ solutions may replace the toxic cyanide baths commonly used in silver electroplating.

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