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Environmentally friendly natural polyhydroxylic compounds in electroless copper plating baths: application of xylitol, D-mannitol and D-sorbitol as copper(II) ligands

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Abstract

The possibility of using xylitol, D-mannitol and D-sorbitol as Cu(II) ligands in electroless copper baths was demonstrated. The ligands mentioned showed good chelating properties for Cu(II) ions in alkaline media ($pH > 11.5$), i.e. under conditions of the use of traditional formaldehyde-containing solutions. Electroless copper plating solutions containing the chelators xylitol, D-mannitol and D-sorbitol are stable and, under the optimal conditions selected, copper coatings up to 3 μm thick can be obtained in 1 h at ambient temperatures.

1. Introduction

Autocatalytic metal ion reduction systems, including electroless copper plating solutions, are widely used to create articles for decorative and functional purposes, i.e. for deposition of metal layers on dielectrics or on conductors of complicated configuration [1–4].

Cu(II) ligands are important components of common formaldehyde-containing alkaline electroless copper plating baths. The compounds used should form Cu(II) complexes stable enough to prevent $Cu(OH)_2$ formation. Since the solubility product of $Cu(OH)_2$ is of the order 10^{-18} [5, 6], the concentration of 'free' (uncomplexed) Cu(II) ions in the pH range 11–14 cannot exceed 10^{-12}–10^{-18} M, respectively.

EDTA (ethylenediaminetetraacetic acid) is currently the most widely used ligand in systems for electroless copper plating [1–4], partly because it has excellent chelating properties over a wide pH range. Its use thus ensures acceptable parameters for the electroless Cu deposition process, but it also creates environmental hazards. EDTA forms stable heavy metal complexes that are highly mobile in the environment, and also increases the total nitrogen content of waste waters [7, 8]. The efficient chemical or biochemical decomposition of EDTA in waste waters remains a serious technological problem.

Alditols (saturated polyhydroxylic alcohols) could provide alternatives to EDTA in electroless copper plating processes. They form very stable complexes with Cu(II) ions in alkaline solutions that result in free Cu(II) concentrations low enough to prevent the precipitation of $Cu(OH)_2$, but do not form metal complexes under the near-neutral pH conditions found in waste-water treatment processes and natural waters [9–11]. In addition, these natural polyhydroxylic compounds are easily biodegradable. Therefore, the use of alditols as environmentally friendly ligands for electroless copper baths is promising.

Among the polyhydroxylic alcohols only glycerol has been widely used as a Cu(II) ligand in electroless copper plating solutions [12–15]. The potential use of higher polyhydroxylic alcohols: meso-erythritol (4 OH-groups), adonitol (5 OH-groups), D-mannitol, D-sorbitol and dulcitol (all with 6 OH-groups), has been briefly described by Ohno [16], who showed that copper plating rates decrease from 1.5 to 0.6 mg cm^2 h^{-1} as the number of OH-groups in the ligands increases from 4 to 6.

The aim of the work presented herein was to evaluate electroless copper deposition in solutions containing xylitol, D-mannitol and D-sorbitol as Cu(II) ligands.

2. Experimental details

Electroless copper plating experiments were carried out for 1 h at 20 °C or 30 °C in 25 ml solution containing: 0.05 M $CuSO_4{\cdot}5H_2O$; 0.10 or 0.15 M Cu(II) ligand (xylitol, D-mannitol or D-sorbitol); and 0.15 M HCHO. Sodium hydroxide was used to adjust the pH to the desired values. In some experiments the concentration of HCHO was also varied. The amount of copper deposited was determined by mass difference. All measurements were repeated at least three times and mean value calculated.

The substrate was a Pt sheet (1 × 1 cm) electroplated with Cu for 10 min from acid copper solution (0.8 M $CuSO_4$ + 0.6 M H_2SO_4) at 1 A dm^{-2}. Before the electroless plating the substrate was activated for 30 s in acid $PdCl_2$ solution (1 g l^{-1}).

Measurements of pH (20 °C) were achieved using a Mettler Toledo MP 220 pH-meter and a Mettler Toledo InLab 410 glass electrode. The calibrations of the pH electrode were carried out using decarbonized solutions of NaOH of various concentrations. Formaldehyde concentrations in the electroless copper plating solutions were determined titrimetrically [17].

3. Results and discussion

3.1. *Electroless copper deposition from solutions containing xylitol as the Cu(II) ligand*

The data for Cu(II) complexation in alkaline solutions of xylitol (an alditol containing five OH-groups) have only recently been published [18]. Xylitol forms three mononuclear copper(II)-hydroxy complexes at high ($\geqslant 10$) ligand-to-metal ratios: $CuXyl(OH)^-$ ($\log \beta = 17.7 \pm 0.5$), $CuXyl(OH)_2^{2-}$ ($\log \beta = 20.2 \pm 0.3$) and $CuXyl_2(OH)_2^{4-}$ ($\log \beta = 22.4 \pm 0.3$). The binuclear complex Cu_2Xyl ($\log \beta = 29.2 \pm 0.3$) is the predominant species at a lower ligand-to-metal ratio (0.5).

These constants provide a prediction that at the Cu(II) concentration (0.05 M) used in our electroless copper plating solutions, xylitol is unable to adequately chelate Cu(II) ions under conditions of excess metal ion. That is, under alkaline conditions (pH 11–14) with excess Cu(II), pCu values are calculated to be lower than those necessary to prevent precipitation, and $Cu(OH)_2(s)$ should form in the solution bulk (Figure 1a, curve 1). The experiments confirmed these predictions. With an increase in xylitol concentration (two- or three-fold excess), pCu rises dramatically (Figure 1a, curves 2 and 3) and $Cu(OH)_2(s)$ no longer precipitates, creating solutions acceptable for electroless copper plating.

The process of autocatalytic reduction of Cu(II)–xylitol complexes by formaldehyde occurs at pH values higher than 12 (Figure 2). The plating rate near the lower pH limit (pH 12.3) is in the range of 0.5–1 μm h^{-1}, depending on the temperature and xylitol concentration. The copper deposition rate increases with increasing pH, reaching maximum values in the pH region 13.2–13.7, and then decreases as the pH is further elevated (Figure 2). The pH dependencies of Cu plating rates show distinct maxima. As the xylitol concentration is increased, these pH maxima move toward higher pH values (cf. Figure 2a and 2b). The thickness of the compact copper coatings obtained under optimal operating conditions in 1 h reaches 2.5–3 μm. The plating solutions are stable and no signs of Cu(II) reduction in the bulk solution were observed.

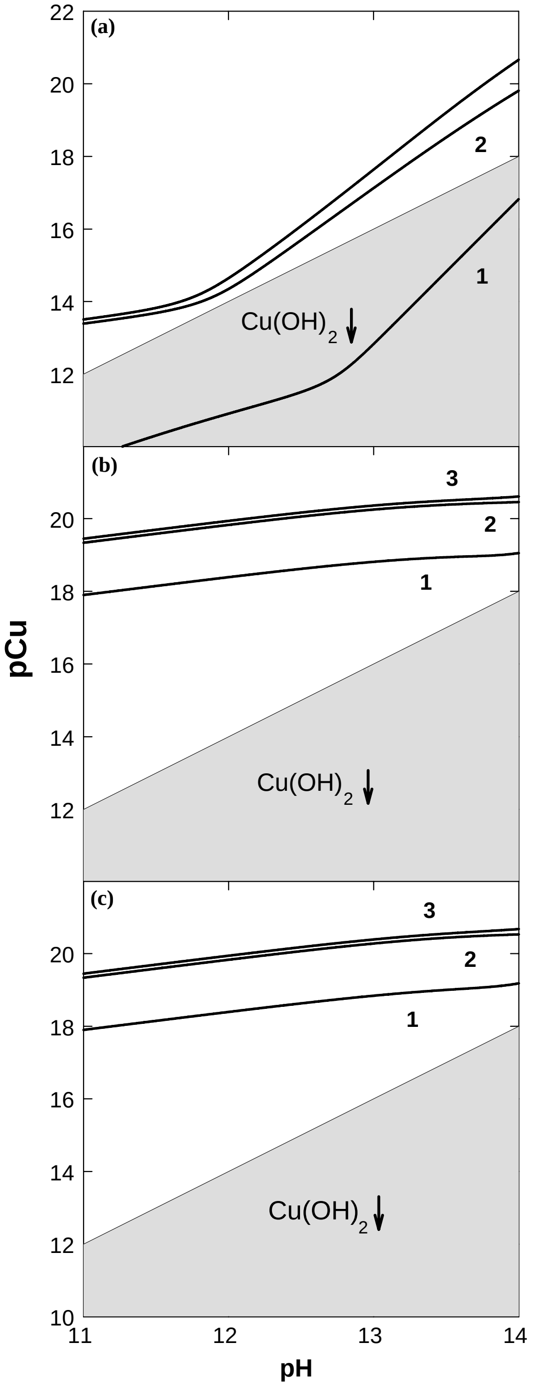

Fig. 1. Relationships of pH to pCu in xylitol (a), D-mannitol (b) and D-sorbitol (c) containing solutions. Solution compositions (M): $CuSO_4$ 0.05; ligands: (1) 0.025, (2) 0.10, (3) 0.15. Filled areas represent regions of $Cu(OH)_2$ precipitate formation.

Comparisons of the Cu deposition rate data with the Cu(II) distributions among the complexes with xylitol (Figure 3), indicate that the plating process begins when the $CuXyl_2(OH)_2^{4-}$ species appear in the solution and the plating rate increases with the concentration of this complex. This suggests that the $CuXyl_2(OH)_2^{4-}$ complex is the principle electroactive species in the catalytic reaction investigated.

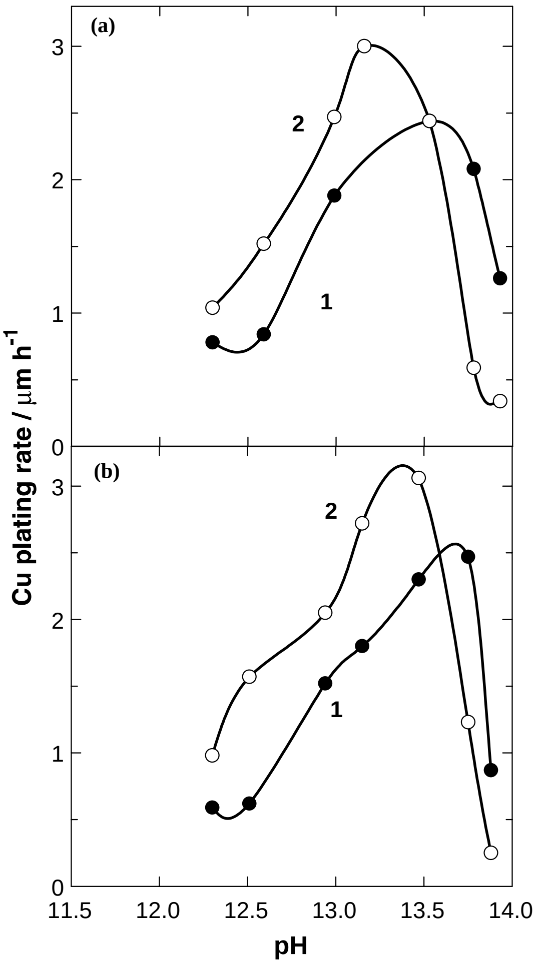

Fig. 2. Dependence of Cu plating rates on pH. Solution compositions (M): $CuSO_4$ 0.05; xylitol: (a) 0.10, (b) 0.15. Temperature (°C): (1) 20, (2) 30.

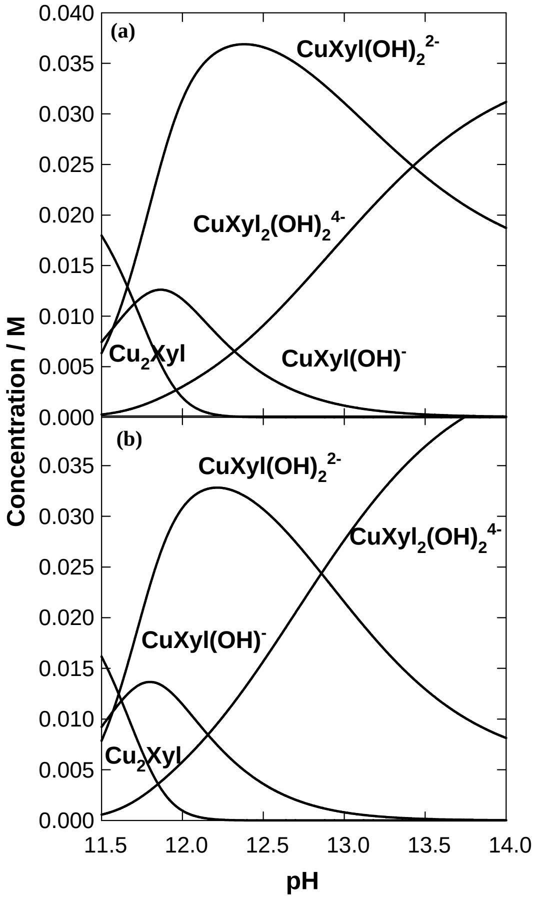

Fig. 3. Distribution at 20 °C. of Cu(II) among the complexes in solutions containing (M): $CuSO_4$ 0.05; xylitol: (a) 0.10, (b) 0.15.

The observation of dramatic decreases in plating rates at higher pH values warrants additional discussion. As the pH is increased above the observed rate maxima, no changes in copper or formaldehyde speciation are expected, i.e. $CuXyl_2(OH)_2^{4-}$ and the methanediol anion form of formaldehyde should continue to dominate the speciation [19, 20]. Thus, the observed rate decreases must be related to the surface state of the deposited copper. The Cu surface obtained at higher pH values is less catalytically active due to the formation of Cu(I) oxy- and hydroxy-species. The formation of such compounds on Cu surfaces was confirmed in investigations of electroless copper plating using other polyhydroxylic ligands – glycerol, saccharose and L(+)-tartrate [21–23]. The Cu(I) species retard the process of autocatalytic reduction of Cu(II) by formaldehyde through retardation of anodic formaldehyde oxidation on the Cu surface [24].

Another reason for the decrease in copper plating rate in strongly alkaline solutions could be a decrease in formaldehyde concentration due to the Cannizzaro reaction. However, formaldehyde determinations have shown that changes in total formaldehyde concentration in electroless copper plating solutions over the 1 h duration of the experiments were not significant (the decrease did not reach 5%), and could not cause a significant reduction in the plating rates.

An increase in temperature from 20 °C to 30 °C increases the maximum copper plating rate by about 20%, and shifts the 'plating rate–pH' curve to lower pH values (Figure 2). Although a higher copper plating rate is observed at elevated temperature for lower pH values, the opposite is true at higher pH values. If the pH is over 13.5, the rate of copper deposition at 30 °C is about half as high as that at 20 °C (Figure 2). This suggests that at elevated temperatures and higher pHs, copper surface passivation is accelerated.

3.2. *Electroless copper deposition from solutions containing D-mannitol as the Cu(II) ligand*

According to a recent investigation of equilibria in alkaline Cu(II)–D-mannitol solutions mannitol behaves as a ligand in a manner somewhat analogous to xylitol [25]. Under conditions of excess Cu(II), the dinuclear complex Cu_2Man is formed ($\log \beta_{Cu_2Man} = 40.5 \pm 0.2$), whereas with ligand excess (tenfold and more), depending on pH and ligand concentration, three complex compounds are formed: $CuMan(OH)_2^{2-}$, $CuMan_2(OH)^{3-}$ and $CuMan_2(OH)_2^{4-}$ with $\log \beta$ values of 19.2 ± 0.3, 19.2 ± 0.4 and 21.1 ± 0.3, respectively.

Comparison of the formation constants for Cu(II) complexes with D-mannitol with those for xylitol complexes points to the similar stability of the complexes, except for the dinuclear species. The stability constant of Cu_2Man is about 11 orders of magnitude higher than that of Cu_2Xyl. The high stability of the D-mannitol complex should allow formulation of electroless copper plating solutions without ligand excess.

Calculations indicate that, in alkaline solutions (pH 11–14), D-mannitol is able to chelate 0.05 M Cu(II) sufficiently to prevent $Cu(OH)_2$ precipitation under conditions of either ligand or copper ion excess (Figure 1b, curves 1–3). Experiments confirmed these predictions, which demonstrates that electroless copper plating solutions using D-mannitol as the Cu(II) ligand without the concentration ratio limitations observed for xylitol.

Two types of solutions with different Cu(II): D-mannitol molar ratios were investigated. In solutions with an excess of Cu(II) ions (Cu(II): D-mannitol molar ratio 2:1), autocatalytic reduction of Cu(II) by formaldehyde starts at pH > 13 (Figure 4a). The plating rate near the lower pH limit (pH ~ 13.5) is lower than 0.5 μm h^{-1}. With the further increase in solution pH, the plating rate rises sharply and, depending on temperature, reaches 1.5–2 μm h^{-1} at a pH near 14. Such a dramatic increase in the rate of the process could be caused by a significant increase in the concentration of OH^- ions, since the total process of autocatalytic Cu(II) reduction occurs with participation of four OH^- ions:

$$\begin{aligned}&\text{Cu(II)–ligand} + 2HCHO + 4OH^- \\ &\xrightarrow{Cu} Cu + H_2 + 2HCOO^- + 2H_2O + \text{ligand} \qquad (1)\end{aligned}$$

The effect of temperature is more pronounced at higher pH values, and the plating rate at 30 °C is about 30% higher than that determined at 20 °C (Figure 4a). It should be noted that, in contrast to the Cu(II)–xylitol system, no passivation effects were observed in this solution.

In the solutions containing two- or three-fold excesses of D-mannitol, the characteristics of electroless copper deposition are similar to those of the Cu(II)–xylitol system. The process of autocatalytic reduction of Cu(II)–D-mannitol complexes begins at pH > 12.5 (Figure 4b and c). The plating rate near the lower pH limit (pH 12.6) is slow (0.1–0.5 μm h^{-1}); lower than that obtained under the same conditions in xylitol-containing solutions. The plating rate increases with pH, reaching maximum values in the pH region 13.5–13.8, and decreases at higher pH. The maximum rate of the process rises slightly with an increase in D-mannitol concentration (cf. Figure 4b and c). Compact copper coatings 2–2.5 μm thick are obtained in 1 h under optimal operating conditions. The effect of temperature is similar to that of the Cu(II)–xylitol system: the plating rate rises with an increase in temperature from 20 °C to 30 °C, the rate enhancement reaching nearly 60% (pH 13.6). The solutions investigated were stable and no reduction of Cu(II) in the bulk solution was observed.

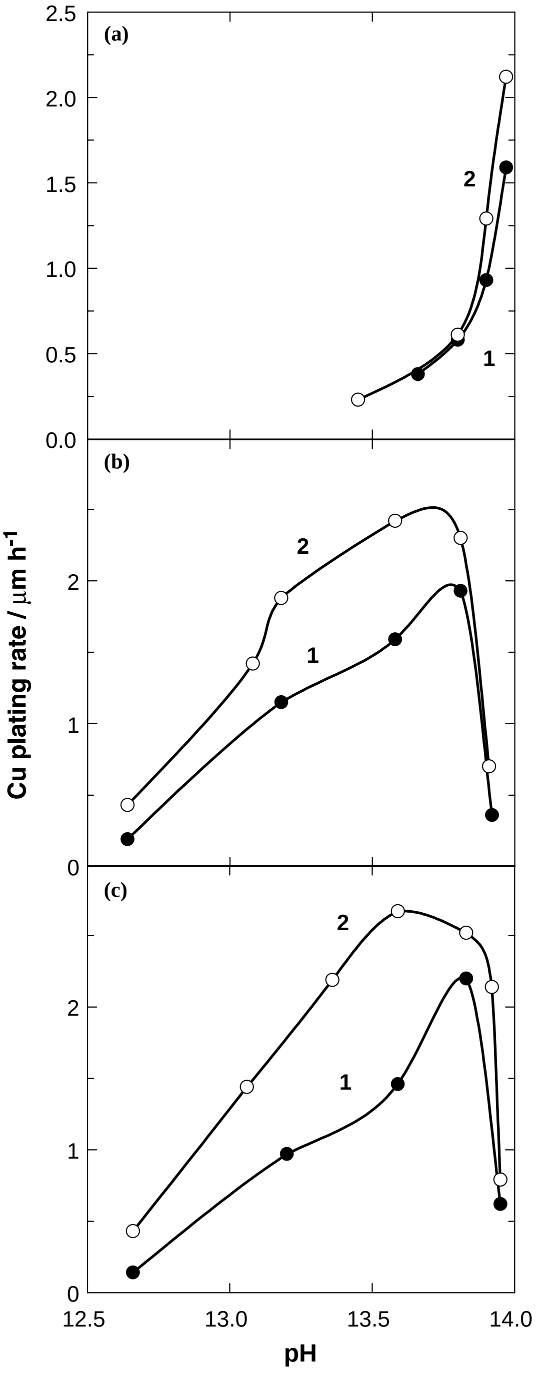

Fig. 4. Dependence of Cu plating rates on pH. Solution compositions (M): $CuSO_4$ 0.05; D-mannitol: (a) 0.025, (b) 0.10, (c) 0.15. Temperature (°C): (1) 20, (2) 30.

Calculations of the distributions of Cu(II) among the complexes with D-mannitol show that Cu_2Man is only complex in solutions with two fold excess of Cu(II) ions, regardless of the pH, i.e. the tetrahydroxycuprate(II) $Cu(OH)_4^{2-}$ [26] does not form under these conditions. The dinuclear complex also predominates in the solutions with an excess of D-mannitol (Figure 5a and b), and only at pHs above 13.5 do the mononuclear dihydroxycomplexes, $CuMan(OH)_2^{2-}$ and $CuMan_2(OH)_2^{4-}$, appear in solution.

It is possible to conclude from the comparison of the pH-dependencies of copper plating rates and of distributions of Cu(II) among the complexes with D-mannitol that the Cu_2Man complex is the electroactive species in the catalytic reduction of Cu(II) by formaldehyde and that it does not inactivate the copper surface during the plating process (see Figure 4a and the data of Figure 4b and c below pH=13.5). The rise in the predominance of the dihydroxycomplexes $CuMan(OH)_2^{2-}$ and $CuMan_2(OH)_2^{4-}$ at pHs over 13.5 coincides with the retardation of the copper deposition process. Apparently, the decrease in plating rate occurs due to the adsorption of these species or/and incomplete reduction of Cu(II) from these complexes with formation of Cu(I) compounds on the Cu surface.

3.3. *Electroless copper deposition from solutions containing D-sorbitol as the Cu(II) ligand*

The data on the composition and stability of Cu(II) complexes with D-sorbitol (isomer of D-mannitol) in alkaline solutions [27] indicate formation of four complex species: Cu_2Sorb, $CuSorb(OH)_2^{2-}$, $CuSorb_2(OH)^{3-}$ and $CuSorb_2(OH)_2^{4-}$, with log β values of 40.7 ± 0.3, 17.9 ± 0.3, 20.1 ± 0.2 and 21.2 ± 0.2, respectively.

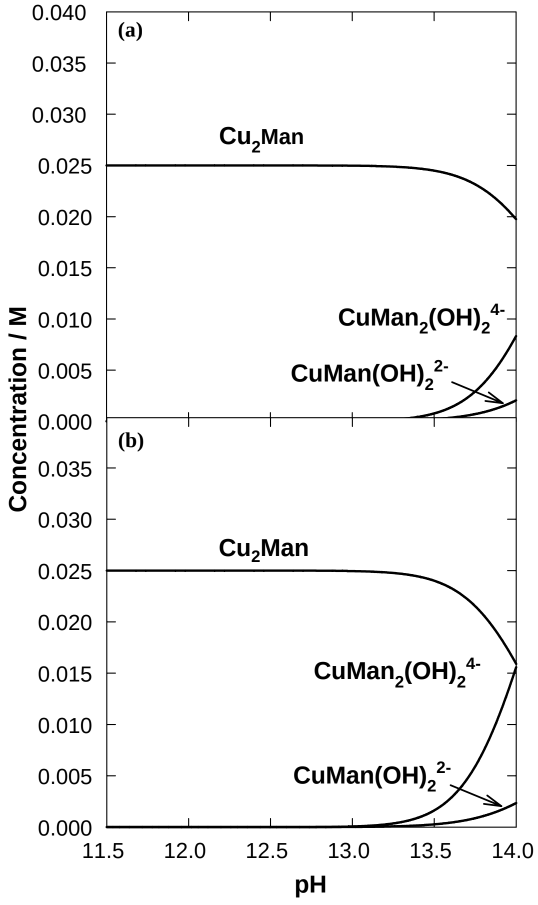

Fig. 5. Distribution of Cu(II) among the complexes in solutions containing (M): $CuSO_4$ 0.05; D-mannitol: (a) 0.10, (b) 0.15. 20 °C.

When comparing Cu(II) complex formation in this system with that of Cu(II)–D-mannitol [25], it is seen that the stoichiometries of the complexes formed are identical and that stabilities of the complexes are comparable. Therefore the complexation of Cu(II) ions in D-sorbitol solutions should be very similar to that in D-mannitol solutions. The pCu data (Figures 1b and 1c) show identical dependences of Cu(II) complexation on pH in alkaline solutions of D-sorbitol and D-mannitol.

Although the chelating properties of D-sorbitol and D-mannitol are similar, the electroless copper plating process from solutions containing these ligands differs considerably. For instance, the copper plating rate is quite low (0.2–0.4 μm h^{-1}) in D-sorbitol solutions with an excess of Cu(II) (Figure 6a), while in the case of D-mannitol the rate reaches 2 μm h^{-1} (Figure 4a). Similar differences are also observed in solutions containing an excess of D-sorbitol. The maximum rate of Cu deposition from D-sorbitol-containing solutions (about 1.5 μm h^{-1}) is lower than that obtained from D-mannitol solutions (about 2 μm h^{-1}). Moreover, in the case of D-sorbitol, the pH at the maximum plating rate is shifted to a lower pH (13.4) when compared with Cu(II)– D-mannitol system (pH 13.8). In the Cu(II)–D-sorbitol system the retardation of the copper deposition rate begins at lower pH values as compared with D-mannitol solutions (cf. Figures 6b, c and 4b, c).

The distribution of Cu(II) among the complexes with D-sorbitol is practically the same as that for D-mannitol (Figure 5), so the same conclusions drawn above for the D-mannitol system about the predominance of the dinuclear complex (Cu_2Sorb) in the electroless deposition process and the role of the mono-nuclear complexes at pHs over 13.5 should be valid for the D-sorbitol system. Rather unexpected results were obtained in the solutions containing excess of D-sorbitol at 30 °C. The copper-plating rate dependence on pH has two maxima (Figure 6b and c). This apparently reflects a complicated picture of changes in Cu surface activity in this system under very high pH conditions.

The observed differences in electroless copper plating behavior in solutions containing either of the two hexitol isomers, i.e. D-sorbitol and D-mannitol, was unexpected. The stoichiometries and stabilities of the Cu(II) complexes with either ligand are similar, and the deprotonation constants of D-sorbitol and D-mannitol are numerically similar ($pK_{D\text{-sorbitol}}$=13.5 ± 0.3 [27] and $pK_{D\text{-mannitol}}$=13.3 ± 0.3 [25]). This implies very similar levels of stoichiometrically identical Cu(II) complex ions in the solutions of either isomer (cf. Figure 1b, c). Thus the observed differences in plating behavior are probably explained by the differences in the structures of D-sorbitol and D-mannitol in solution. It is generally agreed that in aqueous solutions, D-mannitol adopts a planar zig-zag conformation, while D-sorbitol has a sickle-shaped one [28]. Some noticeable differences have been observed in the interactions between these

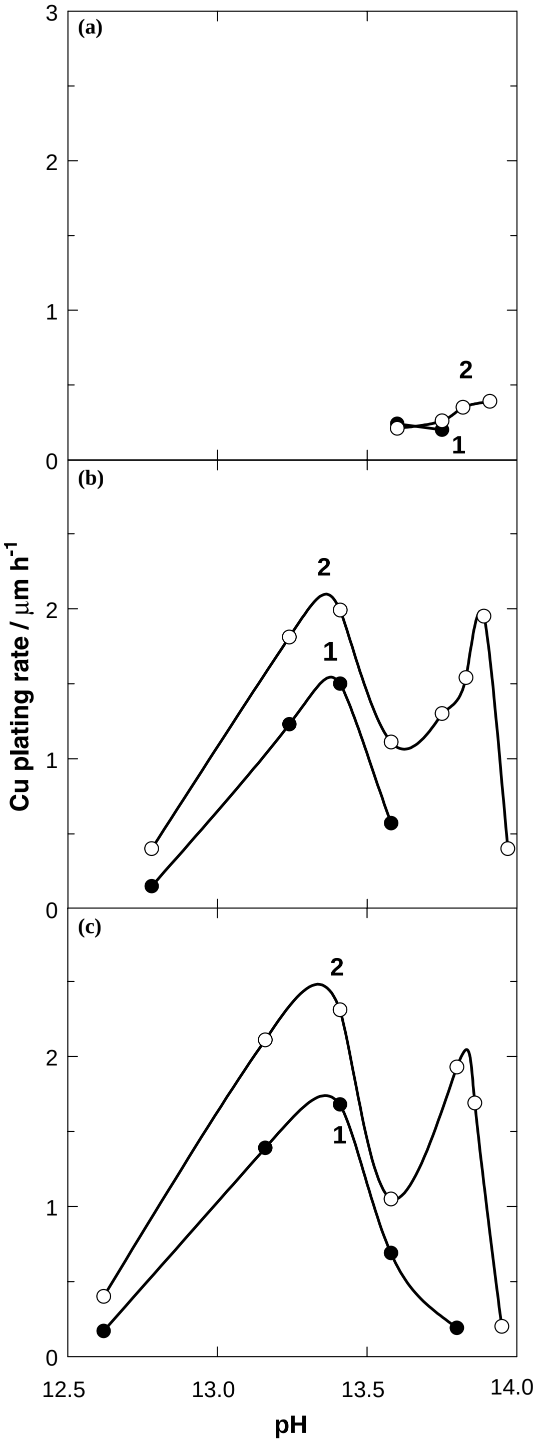

Fig. 6. Dependence of Cu plating rates on pH. Solution composition (M): $CuSO_4$ 0.05; D-sorbitol: (a) 0.025, (b) 0.10, (c) 0.15. Temperature (°C):(1) 20, (2) 30.

stereoisomers and metal surfaces, as well as in electrochemical behavior (adsorption on mercury [29] and gold [30], adsorption and electro-oxidation on platinum single crystal electrodes [31, 32]).

Finally it is necessary to note that copper recovery from the electroless copper solutions containing xylitol, D-mannitol or D-sorbitol as Cu(II) ligands is inherently less complicated than in the conventional EDTA-containing solutions, since the Cu(II) complexes with alditols can be decomposed by simply lowering the solution pH to values less than 9 or 10.

4. Conclusions

This study demonstrated the possibility using xylitol, D-mannitol or D-sorbitol as Cu(II) ligands in electroless copper plating baths. Generally the autocatalytic reduction of Cu(II) by formaldehyde from solutions containing the ligands begins at pHs above 12, accelerates with a further increase in pH, reaches a maximum value between pH 13.2 and 13.7, then slows at higher pH values. Using D-mannitol and D-sorbitol as ligands allowed electroless copper plating to proceed with ligand to Cu(II) ion molar ratio as low as 1:2. It was shown that autocatalytic reduction of Cu(II) occurs from the dinuclear Cu_2Man and Cu_2Sorb complexes even if two- or three-fold excesses of ligand are used.

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